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Synthesized Tannin Foam from Tannin Resole Dehydrated by Hot Air Oven

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A simple method for synthesizing tannin foam (TF) from tannin resole (TR) was studied. Tannin was used as a substitute for phenol with a 10 wt% substitution ratio to form TR. The mixture of TR was dehydrated to get the TR with a solid content of 80% using a hot air oven. The dehydrated TR was used as an essential component for the formation of the TF. The functional groups, density, and compressive strength of the synthesized TF were tested by using an FTIR, ASTM D1622, and ASTM D1621, respectively. From the FTIR spectra, it was found that functional groups of TF were similar to phenol foam (PF). The addition of tannin increased the density and compressive strength of the TF. The density of tannin foam was 90.92 kg/m³, and the compressive strength of tannin foam was 0.25 MPa. Using tannin resole to make synthesized tannin foam proved to be a simpler method in dehydrating resole by hot air oven as compared with the conventional method. Moreover, the thermal performance of the TF was performed, and it was found that the TF showed a similar thermal performance to the PF.

Key Words

Bio-foam, Dehydrated resole, Phenolic, Substituted phenol, Tannin foam

1. Introduction

Phenolic foam is one of the insulating materials used to resist heat transfer into residences ¹⁾. Generally, the phenolic foam is made from phenol, blowing agent, and other additions and cured at different temperatures ²⁾. The phenol is a product from non-renewable petroleum. Many studies were attempted to find alternative materials from natural sources for replacing phenol, such as lignin and tannin, which contain similar phenolic compounds and functional groups as in phenol structure ^{3)~5)}.

Tannin is a component in plants such as bark, leaves, trunks, and fruits. The complex structures of tannin were formed with phenolic compounds and several other macromolecular ⁶⁾. In various applications, tannin was used

to replace phenol. Tannin depolymerized by NaOH/urea was used as a mixer to synthesize tannin resin. The chemical structure of tannin resin contains similar functional groups to those of phenol resin. Thus, tannin has the potential as a substitute for phenol ⁷⁾. Moreover, tannin resin can be used for forming foams. In a study by Li, J. *et al.* ⁸⁾, tannin could substitute up to 30 wt% phenol, and the tannin foam had a compressive strength of 81.53 KPa and thermal conductivity of 0.04345 W/m.K. However, the synthesis of tannin foam from resin generally requires dehydration of the resin by the vacuum reduced pressured method, which requires specific equipment and high energy consumption. The vacuum method is also difficult in upscaling due to the limited capacity.

Inspired by the previous studies, the authors were interested in simplifying TF synthesis from TR by using a hot air oven to dehydrate the resole. The TR was prepared by replacing phenol with untreated tannin of 10 wt% to be used to synthesize tannin foam. The foam was tested for chemical and physical properties and thermal performance.

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2. Methodology

2.1 The synthesis of TR and TF

The scheme of tannin foam synthesis can be seen in Fig. 1. The compositions of resole were shown in Table 1. TR was prepared by mixing phenol with tannin at 10 wt%. The reactor for synthesized resole was set up with a three-necked flask, including a cooling condenser, addition chimney, thermometer, and magnetic stirrer in preheat water bath 85 °C. To prepare TR, 4-g tan-nin, 36-g phenol, 3.6-g NaOH (solution water 50% w/w), and 10-g distillate water were loaded and stirred for 30 min. After that, formaldehyde 62.4-g was dropped with the reactor was stirrer continuously working for 120 minutes. The TR was cooled down for 12 h at room temperature and was adjusted pH to 5.5 ± 0.5 by acetic acid (5 Molar). The tannin resole was dehydrated by hot air oven at 105 °C for 6 hr with a solid content of 85 ± 5 %. The TR was controlled by phenol resole (PR), in which the resole was prepared by only phenol (40-g phenol) without tannin.

The synthesis of tannin foam (TF) made from TR was prepared with phenol foam (PF) derived from PR. The additions of foam were shown in Table 2. The resole was stirred with a blowing agent (hexane), plasticizer (glycerol),

and the crystal liquid mixer (blended catalyst, surfactant, and solvent) vigorously stirred for 1 min. The sample was immediately placed into the preheated oven at 80 °C for curing and forming foam.

2.2 Sample testing

For resoles, the solid contents were determined according to ASTM D4426. The pH of resoles after adjusted by acetic acid was measured by pH meter at room temperature. For properties of foams, the chemical properties were characterized using Fourier Transform Infrared Spectroscopy (FTIR) (Tensor 27, Bruker, German). The densities and compressive strengths of foams were determined according to ASTM D1622 and ASTM D1622, respectively. The iOS operational system (iPhone X) was used for taking the area of porosity of foams over the cross-section with a fixed distance between sample and camera lens of 8 cm. The area of porosity of foams was analyzed using ImageJ software following the procedure described in Table 3. The thermal performance of the foam was studied by the method of Suttaphakdee *et al.* (2017)⁹. The foam was placed on top wooden box $15 \times 15 \times 15$ cm³ for recording inside air temperature.

Fig. 1 Scheme of tannin foam synthesis

Table 1 Chemical compositions for the synthesis of resole

Resoles	Weight (g)				
	Phenol	Tannin	Water	NaOH	Formaldehyde
PR	40	-	10	3.6	62.4
TR	36	4	10	3.6	62.4

Table 2 Composition of mixer for the synthesis of foam

Chemicals	Functions	Weight (g)
Resole	Substance	20
p-Toluene sulfonic acid	Catalyst	2.8
Hexane	Blowing agent	2
Water	Solvent	1.2
Glycerol	Plasticizers	1
Between 80	Surfactant	0.8

Table 3 The procedure of ImageJ analysis for the porosity area of foam

Step	Description
1	Open picture of sample (File > Open) and set distance (Straight > Analyze > Set Scale).
2	Crop area for testing: (Rectangular> Image > Crop).
3	Converted picture as the grayscale (Image > Type > 8 bit).
4	Make the binary of porosity (Process > Binary > Make Binary).
5	Separate porosity and foam (Image > Adjust > Threshold).
6	Analyze the area of porosity of foam (Analysis > Analysis Particles > OK).

3. Results and discussion

3.1 The pH and solids content of resoles

The solid content and pH of the resole were measured. The pH of resoles after adjusting by acetic acid were determined to be 5.38 for PR and 5.48 for TR, respectively. For the same dehydration time for 6 hr, the solid content of PR was approximately 87 % and that of TR was approximately 84%.

3.2 The chemical properties of foams

As shown in Fig. 2, FTIR spectroscopy was used to study the chemical structures of TF and PF. Spectra of all foams showed hydroxyl groups at 3357 cm^{-1} , C-H stretching at $2911\text{--}2871\text{ cm}^{-1}$, and C=O at 1715 cm^{-1} . The signals at 1598 and 1462 cm^{-1} indicated an aromatic ring. The absorption peaks of phenolic C-O stretching appeared at 1219 cm^{-1} . The relation of C-O stretching was detected at 1026 cm^{-1} . The absorption spectra of TF and PF were similar, suggesting that the TF and PF had similar chemical structures and functional groups. In this study, the FTIR spectrum of TF foam corresponded to that of tannin foam made from tannin resole dehydrated by vacuum reduced pressure⁸⁾. It implies that the hot air oven method can be applied instead of the vacuum reduced pressured method to dehydrate resole for industrial sections.

3.3 Density and compressive strength of foams

The physical properties of the foams were presented in terms of density and compressive strength at 10% strain. The TF had a density of 96 kg/m^3 and a compressive strength of 0.2506 MPa , whereas the control foam (PF)

had a density of 35.91 kg/m^3 and compressive strength of 0.0732 MPa . The substitution of tannin increased the density and compressive strength of the foam. Since the molecular weight of tannin (1701 g/mol) is higher than that of phenol (94 g/mol), the substitution of tannin led to the increase in viscosity of the resole. The increasing viscosity retarded foam formation by resisting the expansion of air in the resole⁸⁾. Therefore, the porosity of TF was lower than that of PF, leading to higher density. Moreover, the compressive strength of foam depends on density. Tannin foam with much higher density makes the foam stronger and hence higher in compressive strength¹⁰⁾.

3.4 The area of porosity of foams

The area of porosity of foams was monitored with ImageJ analysis as shown in Fig. 3. The image size of foams is $1 \times 1\text{ cm}^2$. Fig. 3 (a) and (c) reveal cross section of PF and TF, respectively. After thresholding the cross-section images, the red-and-white images of PF and TF were obtained as shown in Fig. 3 (b) and (d). The red color refers to the porosity area of foam. The areas of porosity of foams were obtained as 0.559 cm^2 for PF and 0.443 cm^2 for TF. The porosity area of PF was higher than that of TF, which corresponded to the density results.

3.5 Thermal performance of foams

The TF was installed on a wooden box with the heating on the outside, and so was the PF foam. In this experiment, the outside air temperature was increased from room temperature to 53°C at 120 min during heating. After that, the heating source was turned off for another 120 min.

Fig. 2 FTIR spectra of foams

Fig. 3 Photographs of foams with the area measurement using ImageJ: (a) Raw image and (b) thresholded image of PF, (c) raw image, and (d) thresholded image of TF

Fig. 4 Thermal performance of foams

The temperature variation at the center of a wooden box was displayed as curves in Fig. 4. A slight variation of inside air temperature was observed in the temperature range of 28–29 °C for both PF and TF boxes. This implies that there is no significant change in the inside air temperature observed during the whole experiment. Therefore, the foam substituted by 10 wt% tannin was comparable with phenol foam in terms of heat insulation.

4. Conclusion

The synthesis of TF from TR by replacing phenol with 10 wt% tannin proved that the process could be simplified by the dehydration of resole by using a hot air oven. The FTIR showed that the spectra of TF had a similar chemical structure to PF, and no difference was observed between the dehydration methods using a hot air oven and vacuum evaporator. The addition of tannin increased the density and compressive strength of the TF foam. The use of TF foam as a heat insulator for the

wooden box could reduce the variation of the temperature inside, compared with PF foam. The TF foam could therefore be used for thermal insulation.

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