CHARACTERIZATION AND PROPERTIES OF A LIGNOSULFONATE-BASED PHENOLIC FOAM

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Phenolated lignosulfonate was introduced into the synthesis of phenolic resol with phenol and formaldehyde in an alkaline condition. The modified resol was successfully applied to prepare phenolic foam using appropriate combinations of flowing agents. N-pentane was found to be suitable as the foaming agent. Sulphuric acid (50% aqueous solution, w/w) and Tween-80 were used as catalyst and surfactant, respectively. The obtained foams were characterized by thermogravimetric analysis (TGA), scanning electron microscopy (SEM), friability, and mechanical property tests. The experimental results showed the foam to have lower density, better toughness, and excellent thermal insulation compared to those of foams obtained from conventional resol resin. The properties of phenolated lignosulfonate modified phenolic foam can comply with the required specifications for its practical utilization.

Keywords: Phenolated; Lignosulfonate; Phenolic foam; Characterization; Properties

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INTRODUCTION

Rigid foams are commercial materials of increasing interest. Foams based on metals, ceramics, or polymers are already in industrial production. Their application potential is growing with an average annual growth rate of 20% (Celzard *et al.* 2010). For example, phenolic foams, compared with rigid plastic insulation materials such as polystyrene, polyurethane, and polyethylene, are preferred because of their outstanding fire and chemical resistance, their self-extinguishing character, as well as the absence of harmful smokes when exposed to flame (Auad *et al.* 2007). Consequently, these advantages make it an excellent candidate where fire resistance is critical, such as frozen food industries, building materials, and aircraft, with promising developments in materials and new processing techniques (Li *et al.* 2003).

Phenol and formaldehyde are two main raw materials for phenolic foams production and currently are obtained from fossil resources. The rising cost and foreseeable future scarcity of petrochemicals have prompted researchers to evaluate phenolic foams, using natural products from renewable resources. Lignin can be obtained by different pulping processes, but only lignosulfonates are available in great quantities. The chemical structure of lignin is similar to that of phenol, making it an interesting alternative to replace phenol in phenol-formaldehyde (PF) resin formulation (Forss *et al.* 1979). However, it is estimated that there are only 0.3 reactive aromatic sites available for the formaldehyde condensation for every nine-carbon unit of kraft lignin, which is only one-tenth that of a phenol molecule (Pizzi *et al.* 1989; Marton *et al.*1996). In the early studies, lignin was directly incorporated into phenolic resins, where it served both as a filler and a phenol substitute. Because of its extremely low reactivity, direct use of lignin in preparing adhesives required long pressing times and high pressing temperatures. Therefore, unmodified lignin is usually not commercially attractive for such applications. To overcome this disadvantage, a current trend is to modify the chemical structure of lignin to increase its potential reactive sites toward formaldehyde. Our group (Hu *et al.* 2011) have reviewed methods of improving the reactivity of lignin toward formaldehyde, mainly including demethylation, phenolation, and methylolation. Many reports have been published on the preparation of lignin modified phenol formaldehyde adhesives (Alonso *et al*. 2004; Malutan *et al.* 2008; Lin *et al.* 2010; Vázquez *et al.* 1997). To the best of our knowledge, little has been reported about lignin applications in phenolic foam.

In the present paper, phenolated lignosulfonate modified resol resin was prepared and characterized by Fourier transforms infrared spectroscopy (FT-IR). It was successfully applied to prepare phenolic foam by combining proper curing agent, surfactant, and foaming agent. Thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and evaluation of compressive properties of the modified phenolic foam were carried out. Results were compared with conventional phenolic foam (not containing lignosulfonate) in the formulation, in order to assess its potential as a fire-resistent, non-toxic substitute in fire-critical structural applications.

EXPERIMENTAL

Materials

Lignosulfonate, kindly donated by Feihuang Chemical Company, was dried in an oven at 105°C for 24 h, and kept in a desiccator at room temperature until it was used. Technical grade phenol and 37% formaldehyde (HCHO) were purchased from Ling Fen Company and used as received.

Methods

Phenolation lignosulfonate preparation

A flask provided with a thermocouple, mechanical stirrer, and condenser was charged with 100 g of melted phenol. 20 g of lignosulfonate was added slowly, and the pH of the mixture was adjusted with the addition of sodium hydroxide aqueous solution (30% w/w). The resulting mixture pH was in the range 9 to 10. The mixture was stirred and heated slowly to l00-120^{o}C in an oil bath, then refluxed at temperature for 1 h. The reaction was quenched by cooling to 70^{o}C.

Resol synthesis

Formaldehyde (37% aqueous solution) was slowly dropped into the above phenolated lignosulfonate mixture; the mole ratio of formaldehyde to phenol was 1.7:1. The resinification between phenolated lignosulfonate, phenol, and formaldehyde was conducted with constant agitation at 80°C. When the degree of condensation was appropriate (samples fell into a beaker full of water of 25°C as a thread), the resulting mixture was neutralized to pH 6-7 by addition of sulfuric acid. Finally, volatile products were removed under vacuum until the desired solid content was obtained. Its viscosities were within 4500 to 6000 cP at 25^{o}C, and the solid content was between 75 and 82%.

General procedure for foam preparation

Phenolated lignosulfonate modified resin was prepared as above, with the addition of N-pentane (acting as foaming agent) and Tween-80 (acting as surfactant), which were thoroughly mixed at room temperature using an overhead mechanical stirrer. Continuous stirring of the mixture was continued vigorously for several seconds after sulphuric acid (50% aqueous solution w/w, acting as curing agent) was added until the mixture was homogeneous and became warm. Then the mixture was quickly poured into a square paper box (15×15×15cm) in a pre-heated oven at 70^{o}C. Formation of foam required 10 min, and the complete cure was obtained after 30 min at the same temperature. After cooling down, the foam was removed from the mold to allow characterization. The process was as shown in the flow chart (Fig.1). Foam formulation is listed in Table 1. To allow comparison, conventional resol resin and its foam were prepared in the same way.

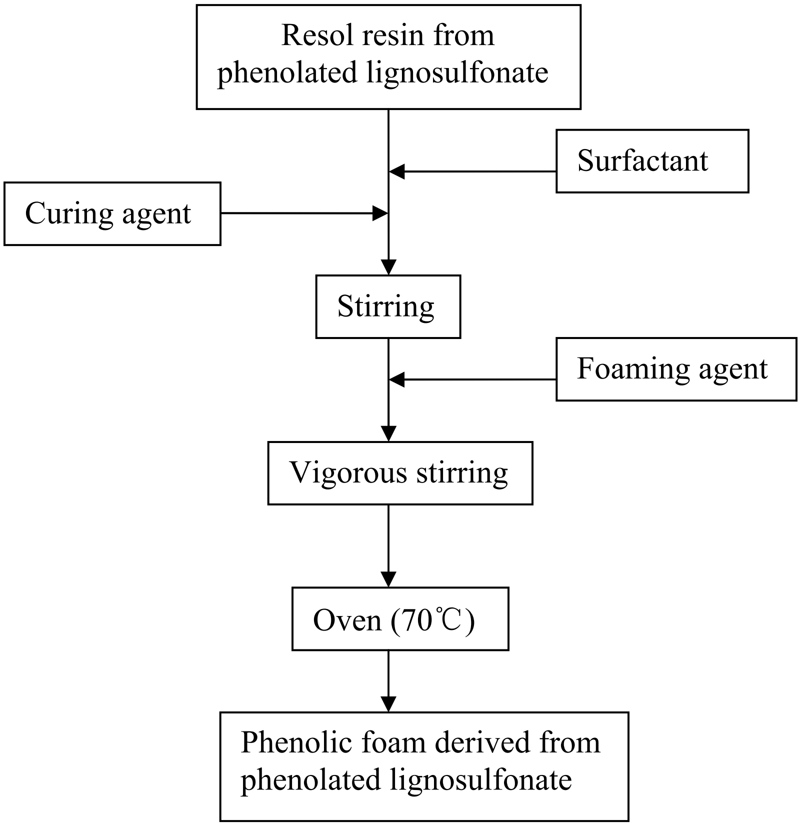


Fig. 1. Sample preparation

Table 1. Combinations of Foaming Agents for Preparing Phenolic Foam

Agents	Combinations(g)
Phenoliated lignosulfonate-based resol resin	100
Blowing agent(N-pentane)	10-12
Surfactant(Tween-80)	3
Catalyst(sulphuric acid, 50% aqueous solution, w/w)	10

Characterization

Infrared spectra

IR spectra of the resol resin (after freeze drying) were obtained using a Nicolet FT- IR 560 spectrometer (Nicolet Co., USA), equipped with a deuterated triglycine sulfate detector. Six-four co-addition scans were made in a frequency range of 4000 to 500 cm^{-1} at a resolution of 4 cm^{-1} at room temperature.

Viscosity

The viscosity was observed with a DV-II+PRO viscometer (Germany, Brookfield Co.) at 25^{o}C and 60%RH.

Solid content

To detect the solid content of the resol resin, the sample was put in an oven at 105^{o}C for 2 h, then taken out and put into a desiccator. The sample was weighed before and after drying. The solid content was calculated as follows:

$$\textit{solid content(g/g)=dried sample(g)/wet sample(g)} \times 100 \qquad (1)$$

Apparent density measurements

Apparent density [ρ=mass (m)/apparent volume (V), g cm^{-3}] was measured on samples of 15 (length)×30(width)×10 (thickness) mm using a foam saw and an electric balance (Shimadzu balance EB-4300DVW). The average caliper values of each part of a sample were measured at three different spots and used to calculate the apparent volume (V). The mass (M) of each sample was weighed using the Shimadzu balance.

Thermogravimetric analysis

In order to determine the thermal insulation of the foam, TG was carried out using a thermogravimetric analyzer instrument STA409 (Germany, Netzsch Co.). The temperature range in the experiment was 30 to 800^{o}C at a heating rate of 20^{o}C/min using nitrogen at a flow rate of 20 mL/min.

Friability property measurements

Friability was measured in accordance with ASTM C421. Twelve foam cubes with 25.4 mm on each side were mixed with twenty-four oak cubes with 19.0 mm on each side. In a custom-made tumbling box, all cubes were tumbled for 10 min at 60 rpm, and each sample was weighed to an accuracy of 1 mg before and after tumbling.

Morphology

After gold sputtering on the foam samples, they were examined for morphological details with an SEM instrument 3400N (HITACHI Co., Japan) with an acceleration voltage of 15.0kV. The dried samples were examined for morphological details with an FEI quanta 200 SEM instrument with an acceleration voltage of 30 kV and magnification of 3000.

Mechanical property measurements

The sample size was 50 (length)×50 (width)×50 (thickness) mm. Compression strength was measured using an electronic universal testing machine CMT4304 (China, Xinsansi Co.) at 25°C, in the direction perpendicular to the foam rise at a constant crosshead speed of 2 mm/min. The compressive strength of the foams was determined when deformation reached 10% of its original value, according to Chinese National Standard (GB8813-88).

RESULTS AND DISCUSSION

FT-IR Analysis

FT-IR spectroscopy is a valuable tool to establish evidence of resinification, and it was also used to determine the functional groups of the resin. Figure 2 shows the FT-IR spectroscopy of the phenolated lignosulfonate modified resol resin. The stretching vibration absorption band at 3348.2 cm^{-1}, corresponding to hydroxyl groups, as well as the peaks at 1605 cm^{-1}, 1514 cm^{-1}, and 1426 cm^{-1} were attributed to aromatic ring vibrations, bands at 1455 cm^{-1} and 1372 cm^{-1} were due to the bending vibrations of CH_2, and the absorption band at 1030 cm^{-1} was attributed to hydroxymethyl groups.

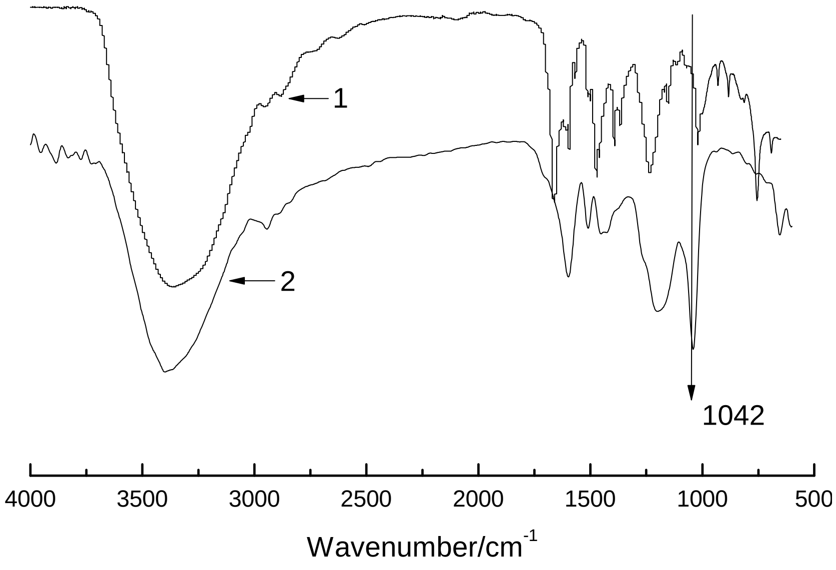


Fig. 2. FT-IR spectra of modified PF resin (1 - phenolated lignosulfonate modified resol resin, 2 - lignosulfonate)

A clear peak at 1042 cm^{-1} was the sulfonate group, as shown in curve 2 in Fig. 2; during the phenolation and resinification process, the peak completely disappeared, indicating that the sulfonate group was effectively cleaved. The band at 1233 cm^{-1} was assigned to the phenlolic hydroxyl group. The peak at 1680 cm^{-1} was due to >C=O stretching vibration in aldehyde, which overlapped the benzene ring skeleton stretching vibration. From the above FT-IR data it was observed that the phenolated lignosulfonate was incorporated into the resin. The absorption bands were assigned as suggested by other researchers (Zhao *et al.* 2001; Tan *et al.* 2001).

Thermal Analysis

The thermal resistance properties of the phenolic foam derived from phenolated lignosulfonate modified resol resin were assessed by thermal gravimetric analysis (TGA) technique. Figure 3 depicts the TGA results for foams including conventional and modified phenolic foam. From the weight loss curve, conventional and modified phenolic foam both thermally decomposed in three temperature regions: 100-200^{o}C was the first thermal decomposition of the crosslinked foam, probably due to the removal of some low weight molecules, such as free phenol, formaldehyde, and water. What's more, closed cell walls broke and gas was released from the void spaces during the heating process, and just a little lost weight could be observed, which indicates that the foam's crosslinked network could not be destroyed in that range of heating. Mass loss in the range 200 to 500^{o}C was attributed to the second thermal decomposition of the crosslinked foam, mainly from the releasing of HCHO and H_2O, derived from the rupture of weak bonds (such as methylene bonds or ether bonds) and conversion of these into more stable structures (Sun *et al.* 2007). The major structural disintegration for modified foam occurred at 443^{o}C, while it took place at 267^{o}C in the case of conventional foam. The 176^{o}C increase in thermal stability could be due to the large amount of rigid structure, caused by the rich benzene ring in modified foam.

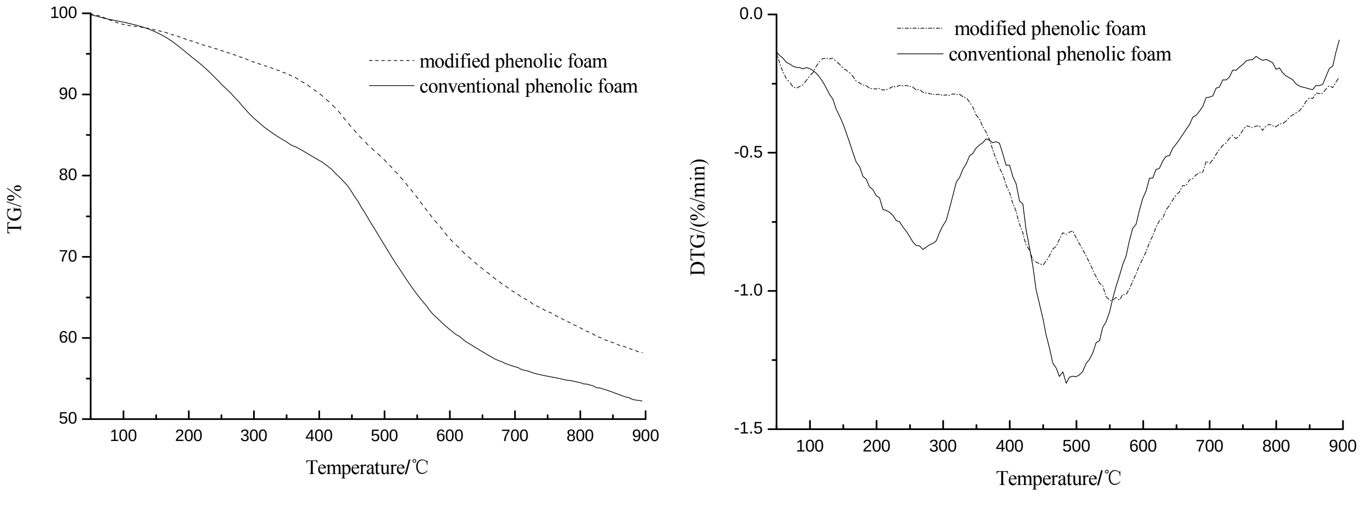


Fig. 3. TG and DTG thermogram of phenolic foam

Modified foam weight loss was about 15.0%, and for conventional foam it was about 23.6%, which means that a 9.6% decrease could be obtained. In the range 500 to 800^{o}C, the third phase of thermal decomposition of the crosslinked foam, a sharp weight loss was due to the further degradation of foam to carbonaceous structures. As clearly shown from the TG profiles, with the introduction of lignosulfonate into the resol resin, the thermal resistance of foam increased, which was demonstrated by higher decomposition temperature and the carbon residue at a lower temperature. For instance, conventional phenolic foam T_D (decomposition temperature in the three stage) was 483.77^{o}C, versus modified phenolic foam T_D (decomposition temperature in the three stage) was 556.83^{o}C. Meanwhile, the carbon residue at 800^{o}C was about 54.5% for the reference phenol 100% foam, compared with 61.2% for the foam containing 20% phenolated lignosulfonate.

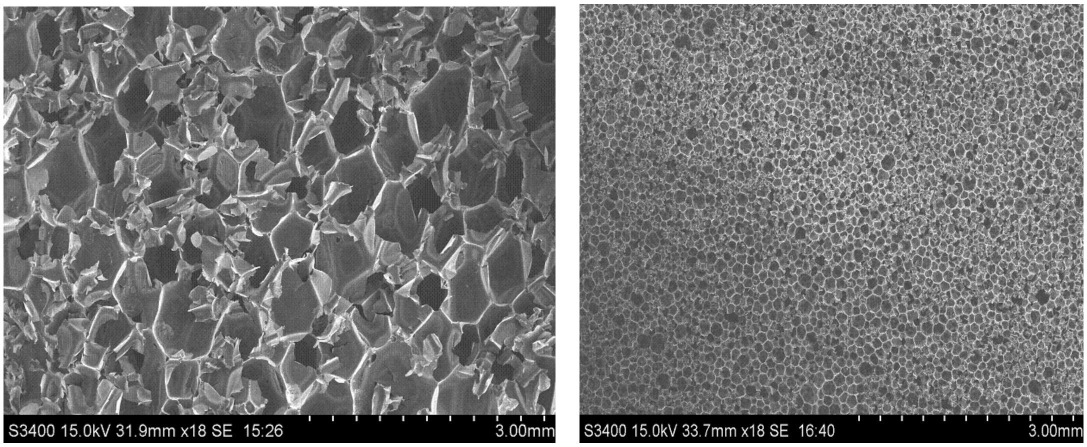
Morphology

Friability is an important property of low-density foams. For phenolic foam with a density below 100 kg/m^3, the friability is so high that severe problems arise in production and applications. For example, the friability of phenolic foam reportedly causes dust pollution in production areas and difficulties in bonding to other materials (Shen *et al.* 2003).

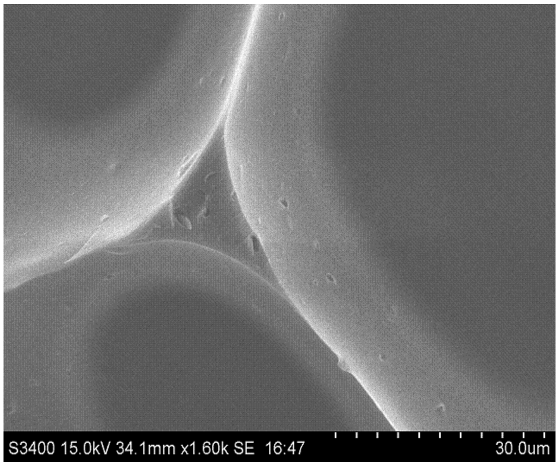
The surface morphologies of conventional and modified phenolic foam, shown in Fig. 4, can reflect the friability property. As shown in these pictures, the conventional phenolic foam (a) surface was much more irregular and there were numerous fragments on it, which indicated its friability. Under the same magnification, the cell of foam (b) shows a uniform dispersion of spherical cells and amazingly smaller cell diameter. What’s more, it had nearly no fragments, which demonstrated that the introduction of phenolated lignosulfonate into phenolic resin can toughen the phenolic foam and make the cells more regular, which is in accordance with the friability test result. The mass loss dropped from 25% for conventional phenolic foam, to less than 19.5% for the modified foam with phenolated lignosulfonate. The improvement implies that the change in friability is associated with an increase in toughness for the modified foam. Dimples on the cell walls represent the areas of continuous, thin polymer films, which form the walls that enclose the cells (Auad *et al.* 2007). Foam (c) showed that the cell walls were extremely thin and smooth, and the diameters were estimated to be less than 2 μm. The angle between three cell walls was almost 120°, which also evidenced the regularity of phenolic foam (b).

Mechanical Properties

The deformation behavior of cellular materials under compressive loading has been well described and analyzed (Tondi *et al.* 2009; Celzard *et al.* 2010; Gibson *et al.* 1997). Like most plastic foams when subjected to compressive loading, phenolic foam exhibits a multi-stage deformation response. As shown in Fig. 5, the initial part of the compressive stress-strain response is revealed, which is the portion of the deformation response that is most relevant for engineering applications, including the key parameters of compressive modulus and strength (Shen *et al.* 2003). The data are summarized in Table 2.



(a) conventional phenolic foam **(b) modified phenolic foam**



(c) magnification of modified phenolic foam

Fig. 4. SEM micrograph of phenolic foams

Lignosulfonate introduction into phenolic foam resulted in a great enhancement in compression properties. Phenolated lignosulfonate (20%, based on phenol weight) caused striking increases in modulus and strength of phenolic foam. The modulus rose to almost nine times the value for conventional phenolic foam, and this was accompanied by a six-fold increase in strength, as shown in Fig. 5. The fact that the effectiveness of phenolated lignosulfonate in enhancing compressive properties exceeded that of conventional phenolic foam can be attributed partly due to the alkyl side chain in the lignosulfonate structure. The alkyl side chain has linear structure and contributes to toughness to a greater degree than a benzene ring by itself (having certain rigidity). Thus, foam derived from lignosulfonate enhanced compressive properties, gave rise to more regular cells, and there was less mass lost.

Data from Table 2 can be used to compare phenolic foam with other commercially available polymer foams. The modified phenolic foam could achieve a comparable level of strength of others, if they have the same density, which indicates that phenolated lignosulfonate modified phenolic foam can be competitive with these structural foams in certain engineering applications, particularly those applications requiring fire resistant properties.

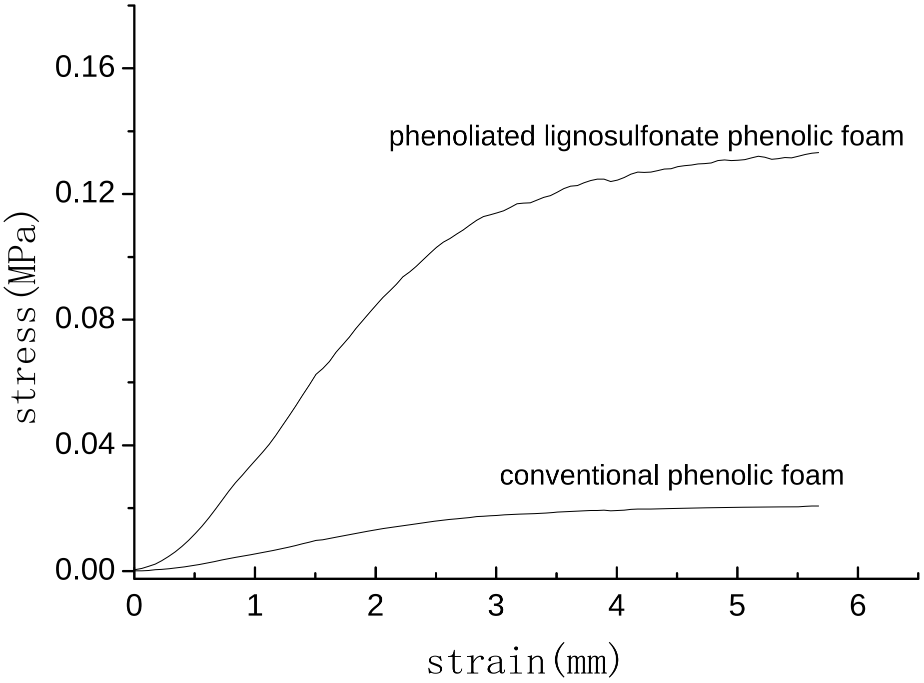


Fig. 5. Compressive stress–strain relationships of phenolic foams. Loading direction is parallel to the foam rise direction

Table 2. Compressive Properties of Foams

Foam formulations	Modulus/Mpa	Density/Kg.m^{-3}	Strength/Mpa
conventional	0.25	35.83	0.02
modified	2.18	28.55	0.15

CONCLUSIONS

The use of modified lignin is an interesting approach for increasing the usage of renewable resources. Lignin is thus very attractive to many industries, as it is a potential source of bio-phenol as a substitute for petroleum-based phenol in the manufacture of phenolic resins.

The utilization of lignosulfonate in the modified phenolic foam is approached in three steps. Initially, the lignosulfonate is modified by phenolation, and immediately formaldehyde is dropped in to formulate the modified resol resin. At last, surfactant, curing agent, and foaming agents are combined with the above resol resin to obtain the modified phenolic foams.

The resulting phenolic foams, when tested for compression, friability, thermal resistance, and morphology, are fully comparable with those of their phenolic counterparts. The present work showed that modifying materials based on lignin can compete with synthetic modifiers for most of traditional applications.

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