

Phenolic Foam Reinforced by Cedar's Resin

Ramzy Hamed¹, Yolla Kazzi² and Houssein Awada^{3*}

¹Faculty of Public Health, Lebanese University, Shouf, Mounty Lebanon, Lebanon.

²Faculty of Sciences, Lebanese University, Hadath, P.O.Box 13-5789, Beirut, Lebanon.

³Centre d'innovation en Ébénisterie et meuble (Inovem), Cegep de Victoriaville 765, rue Notre-Dame Est, Victoriaville (Québec), G6P 4B2, Canada.

Authors' contributions

This work was carried out in collaboration between all authors. Authors RH and YK designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Author HA managed the analyses of the study and the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Recently phenolic foams have been received much attention because of their excellent properties including flame resistance, low density, high thermal stability over a broad temperature range and low generation of toxic gases during combustion. Cedar resin was used as a toughening agent to modify the brittleness of phenolic foam. The cedar resin was first introduced to the phenol formaldehyde resin. The mixture was successfully used to prepare phenolic foam using appropriate combinations of flowing agent. Benzene Sulfonic acid was employed as a curing agent. Orthophosphoric acid and nonionic surfactant polyoxyethylene were used as foaming agent and surfactant respectively.

The mechanical properties results showed that the incorporation of cedar resin into phenolic foam dramatically improved the compressive strength indicating the excellent toughening effect of cedar resin. In addition this property is depended to the percentage of the cedar resin. The apparent density data indicated that the addition of cedar resin can increase the apparent density of phenolic foam.

*Corresponding author: E-mail: awada.houssein@cegepvicto.ca;

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1. INTRODUCTION

Phenolic foam (PF) receives much attention in industrial fields such as building materials for civil construction [1]. Phenol and formaldehyde are two main raw materials for phenolic foams productions and currently are obtained from petroleum [2]. The use of petroleum-based materials can lead to environmental problems because they are non-recyclable and non-degradable [3]. Society is more and more concerned about safety and health issues, while working towards sustainability [4]. Therefore, reinforced PF with renewable polymers are increasingly being used as environmentally friendly composite materials [5,6,7,8]. Phenolic foam was also prepared from a sustainable process [9].

Compared with rigid plastic insulation, materials such as polystyrene [10], polyurethane [11] and polyethylene, PF are preferred because of their excellent properties including fire resistance, low density, high durability, chemical resistance and sound insulation [12,13]. Nevertheless its mechanical properties, particularly brittleness, restrict its application and scientists have made many efforts to improve its toughness. Many reports were published on the preparation of reinforced PF. For example, the use of carbon nanoparticles [14] modified lignin [15,16,17] cardanol [18] and dicyandiamide [19]. In addition, different types of organic and inorganic fillers were used to improve the strength and stiffness of PF [20-22].

Cedar resin has been found to contain essential components such as resin acids, and fatty acids. These weak acids can react with alumina powder to produce a blowing gas H_2 and promote rapid curing during the preparation of the foam. Moreover, the presence of these weak acids allows the decreasing of the mineral phosphoric acid using during the foam process. Furthermore, we can prevent the metal corrosion during the foam process. In addition, cedar resin is a renewable biosourced product.

To the best of our knowledge, little has been reported about the application of cedar resin in phenolic foam.

In the present paper, cedar resin was collected; it was successfully used to prepare phenolic foam modified in varying densities in the range of 30 to

500 kg/m^3 , and by combining proper curing agent, surfactant and foaming agent. Finally, phenolic foams, with increasing content of resin were prepared. The mechanical (the compressive) property, the apparent density and the water absorption were measured.

2. MATERIALS AND METHODS

2.1 Materials

Phenol, formaldehyde, barium hydroxide ($Ba(OH)_2$), benzenesulfonicacid (B.S.A.), ethylene glycol, orthophosphoric acid (OPA), nonionic surfactant polyoxyethylene (OP-7) and alumina powder were purchased from Sigma Aldrich. All of these products were used as received. Cedar resin was collected in Lebanon Mountain and kept in a desiccator at room temperature until it was used.

2.2 Methods

2.2.1 Cedar's resin purification

The purification of the cedar resin involved two steps. In a first step, the resin was heated in hot water bath (70-80°C) until the viscous phase was reached. Then it was filtrated to eliminate impurities. In a second step, the resin was dissolved in acetone for five minutes at 70°C-80°C and then it was filtrated to remove the remaining impurities from natural resin. The remaining acetone was removed by evaporation. Each step of purification was repeated two times.

2.2.2 Foam preparation

Phenol formaldehyde oligomer PFO (Resol brand 309 is a product of the condensation of 1 mole of phenol with 1,5 mole of formaldehyde in the presence of $Ba(OH)_2$ as catalyst at 70°C during 2h in a bath oil.

Cedar's resin was added to the PFO, at different amounts (5, 10, 20 30 40 and 50 wt%), using an overhead mechanical stirrer, in the presence of alumina powder and OP-7 (surfactant agent). Stirring was continued vigorously for two minutes until the mixture became homogeneous.

Then orthophosphoric acid and the benzenesulfonicacid (dissolved in ethylene glycol (7:3) in weight) were added to the mixture and stirred for 60 seconds. The mass amounts (wt%)

Table 1. Experimental conditions used for the preparation of the different samples (S) tested in this study

Component	S1	S2	S3	S4	S5	S6	S7
Phenolic resin	100	95	90	80	70	60	50
Cedar resin (wt% to phenolic resin)	0	5	10	20	30	40	50
Surfactant OP-7 (wt% to PF)	3	3	3	3	3	3	3
Alumina powder (wt% to PF)	0.8	0.8	1	1	1.2	1.5	2
Benzenesulfonicacid in ethylene glycol (7:3 in weight) (w% to PF)	5	5	5	5	5	5	5
Orthophosphoric acid (OPA) (wt% to PF)	4	4	3.5	3.5	3	3	3

of the different chemicals were fixed to the cedar resin and phenol formaldehyde weight. Control sample (without cedar resin) was prepared. Above Table 1 represents the different specific conditions used in this study. The homogeneous mixture was quickly poured into a cubic (30 x 30 mm) cardboard mold. Formation of foam required 3 min.

2.3 Characterization

2.3.1 Mechanical property measurements

The mechanical property measurement (compression strength) was performed on a Instron equipment (British Co). Compressive force (N) values were collected by the "Instron Bluehill" program. The sample dimensions were 30 x 30 x 30 (mm). A load was applied, at a constant rate of 20 mm/min, until it was reduced to 30% less of its initial height. Each result was replicated five times.

The compressive strength of the foams is given by the following expression.

$$\sigma = F/S \text{ with}$$

σ : Modulus compressive strength (Pa)
 F: Compressive force (N)
 S: surface area m²

2.3.2 Water absorption and density measurements

Water absorption is used to determine the amount of water absorbed. For the water absorption test, the samples were dried in an oven at approximately 60°C. Weigh each 12 hours. Samples are dry when the weight is constant for two consecutive readings. Once a constant weight value is obtained, the sample is placed in a desiccator to cool. Immediately upon cooling, the samples were weighed. The materials were then emerged in water at room temperature (23°C). Weigh each 12 hours. Once

a constant weight value is obtained the weight is measured. Before each measuring, water was removed from the surface of the sample with a towel before measuring.

Water absorption of the cubic foam sample was measured in function of the cedar resin contents. Water absorption is expressed as modification in weight percent.

$$\text{Percent Water Absorption (W\%)} = \frac{[(\text{Wet weight} - \text{Dry weight}) / \text{Dry weight}] \times 100}{1}$$

2.3.3 Volumetric mass density measurements

The volumetric mass density [$\rho = \text{mass (m)}/\text{volume (v)} \text{ (g/cm}^3\text{)}$] was measured on cubic samples of 30±0.05 mm using a high precision balance (Shimadzu balance EB-4300 DVW). The dimensions of the sample were verified at three different locations and used to calculate the volume (v).

3. RESULTS AND DISCUSSION

3.1 Compressive Strength

Pure and modified phenolic foams were successfully fabricated. The results of compressive strength measurements as a function of the cedar resin are presented in Fig. 1.

The compressive strength of pure phenolic foam is 300 KPa. After the addition of the cedar resin, the curve shows that the compressive strength of phenolic foam modified with cedar resin was divided into two stages. In the first stage, the compressive strength increased as the cedar resin percentage increased. A significantly improvement was observed when 5% of cedar resin was used. The maximum value of σ is observed when 20% of cedar resin (550 KPa) is administered. This significant improvement may

be attributed to two reasons: the flexibility of the cedar resin-phenolic foam and the decrease in the open structure.

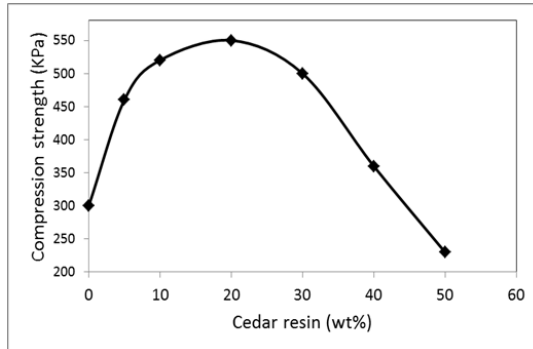


Fig. 1. Compressive strength of phenolic foam samples in function of the cedar resin (% in weight)

In a second stage, a decrease in the compressive strength was observed. This decreasing can be correlated to the saturation of the foam pore by the presence of the cedar resin.

Even a 40% of cedar resin we observed that the measured value of the compressive strength was also higher than of the pure phenolic foam.

This result showed the possibility of replacing a high amount of the phenolic foam (petroleum source) with an ecofriendly ingredient (cedar resin). The obtained reinforced foam can be considered as environmentally friendly composite materials. In addition, we improved the compressive strength of the PF. In addition, these results indicate that the cedar resin can improve the compressive strength of the phenolic foams significantly, and the appropriate content should be below 20% in weight.

3.2 Volumetric Mass Density

The volumetric mass density of the pure phenolic foam and of the phenolic foam modified with the cedar resin was measured. The results are presented in Fig. 2.

The volumetric mass density of pure phenolic foam is 40 Kg/cm³. After the addition of the cedar resin, the curve shows that the volumetric mass density of phenolic foam was increased when the cedar resin percentage increased. This result can be related to the high viscosity of the cedar resin and the saturation of the foam open structure. It is also noticeable that a high value of density can alter the use of phenolic foam. The

amount of the cedar resin will be depending on the final use of the modified foam. A typical formulation containing 5% in weight of cedar resin can be used to obtain modified phenolic foam with a low density value. On the other hand, formulation containing 20% in weight can be used to obtain modified phenolic foam with a high amount of renewable component.

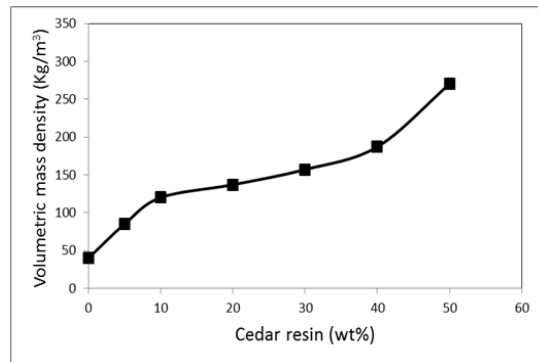


Fig. 2. Volumetric mass density of phenolic foam samples as a function of the cedar resin (% in weight)

3.3 Water Absorption

Finally, the water absorption of the pure phenolic foam and of the phenolic foam modified with the cedar resin was measured. The results are presented in Fig. 3.

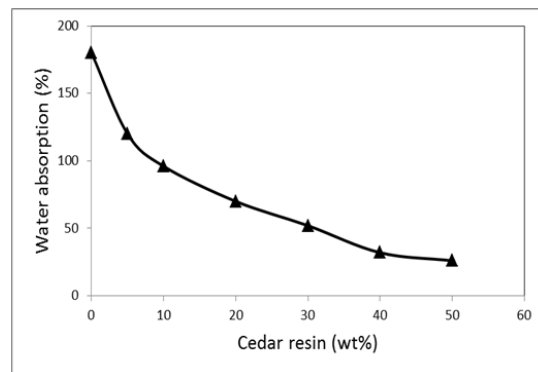


Fig. 3. Water absorption (%) of phenolic foam samples in function of the cedar resin resin (% in weight)

Increasing content of cedar resin from 0% to 50% has decreased the water absorption demonstrating the feasibility of this approach to improve the resistance to water absorption compared to conventional phenolic foam (not containing cedar).

4. CONCLUSION

In this work, cedar resin was used to reinforce phenolic foam. The introducing of 40%, in weight, of the cedar resin has significantly improved both the mechanical properties and the resistance to water absorption of the foam. Nevertheless, the presence of the cedar resin increased the density. Depending on the final application (high or low density), the amount of cedar resin will be adjusted. A typical formulation containing 5% in weight of cedar resin can be used to obtain modified foam with a low density value. On the other hand, formulation containing 20% in weight can be used to obtain modified foam with a high amount of biosourced polymer. Effort should be done during the preparation in order to optimize the conditions requested to control the density.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

- Sun ZX, Wang L, Li DF. Study of preparation and property of phenolic foam. *China Plastics Industry*. 2007;35(8):46-49.
- Hu L, Zhou Y, Zhang M, Liu R. Characterization and properties of a lignosulfonate-based phenolic foam. *BioResources*. 2012;7(1):554-564.
- Awada H, Montplaisir D, Daneault C. The development of a composite based on cellulose fibres and polyvinyl alcohol in the presence of boric acid. *BioResources*. 2014;9(2):3439-3448.
- Awada H, Elchinger PH, Faugeras PA, Zerrouki C, Montplaisir D, Brouillette F, Zerrouki R. Chemical modification of kraft cellulose fibres: Influence of pretreatment on paper properties. *BioResources*. 2015;10(2):2044-2056.
- Bledzki AK, Gassan J. Composites reinforced with cellulose based fibres. *Prog. Polym. Sci*. 1999;24(2):221-274.
- Chai WL, Chow JD, Chen CC, Chuang FS, Lu WC. Evaluation of the biodegradability of polyvinyl alcohol/starch blends: A methodological comparison of environmentally friendly materials. *J. Polym. Environ*. 2009;17(2):71-82.
- Faruk O, Bledzki AK, Fink HP, Sain M. Biocomposites reinforced with natural fibers 2000-2010. *Progress in Polymer Science*. 2012;37(11):1552-1596.
- Huang X, Netravali A. Biodegradable green composites made using bamboo micro/nano-fibrils and chemically modified soy protein resin. *Composites Science and Technology*. 2009;69(7-8):1009-1015. DOI:org/10.1016/j.compscitech.2009.01.014
- Bernardini J, Licursi D, Anguillesi I, Cinelli P, Coltelli MB, Antonetti C, Galletti AMR, Lazzeri A. Exploitation of *Arundo donax* L. Hydrolysis residue for the green synthesis of flexible polyurethane foams. *Bioresources*. 2017;12(2):3630-3655.
- Ozkan DB, Oran C. Optimization of insulation thickness for different glazing areas in buildings for various climatic regions in Turkey. *Applied Energy*. 2011;88(4):1331-1342. DOI: 10.1016/j.apenergy.2010.10.025
- Sarier N, Onder E. Thermal characteristics of polyurethane foams incorporated with phase change materials. *Thermochimica Acta*. 2007;454(2):90-98. DOI: org/10.1016/j.tca.2006.12.024
- Auad ML, Zhao L, Shen H, Nutt SR, Sorathia U. Flammability properties and mechanical performance of epoxy modified phenolic foams. *J. Appl. Polym. Sci*. 2007;104(3):1399-1407. DOI: 10.1002/app.24405
- Shutov FA. *Integral structural polymer foams. Technology, Properties and Applications*; 1986.
- Song SA, Chung YS, Kim SS. The mechanical and thermal characteristics of phenolic foams reinforced with carbon nanoparticles. *Composites Science and Technology*. 2014;103:85-93. DOI:org/10.1016/j.compscitech.2014.08.013
- Alonso MV, Oliet M, Rodriguez F, Astarloa, G, Echeverria JM. Use of a methylolated soft wood ammonium lignosulfonate as partial substitute of phenol in resol resins manufacture. *Journal of Applied Polymer Science*. 2004;94(2):643-650. DOI: 10.1002/app.20887
- Lin ZX, Ougang XP, Yang DJ, Deng YH, Qui XQ. Effect of hydroxyl methylation of lignin on the properties lignin-phenol formaldehyde resins. *Wold Sci-tech R&D*. 2010;32(3):348-351.
- Hu L, Zhou Y, Liu R, Zhang M, Yang X. Synthesis of foaming resol resin modified with oxidatively degraded Lignosulfonate. DOI:org/10.1016/j.progpolymsci.2012.04.003

- Industrial Crops and Products. 2013;44: 364–366.
DOI: org/10.1016/j.indcrop.2012.11.034
18. Liang B, Li X, Hu L, Bo C, Zhou J, Zhou Y. Foaming resol resin modified with polyhydroxylated cardanol and its application to phenolic foams. Industrial Crops and Products. 2016;80:194–196.
DOI: org/10.1016/j.indcrop.2015.11.087
19. Gao M, Wu W, Wang Y, Wang Y, Wang H. Phenolic foam modified with dicyandiamide as toughening agent. Journal of Thermal Analysis and Calorimetry. 2016;124(1): 189–195.
DOI: 10.1007/s10973-015-5156-1
20. Desai A, Auad M, Hongbin S, Nutt SR. Mechanical behavior of hybrid composite phenolic foam. Journal of Cellular Plastics. 2008;44(1):15-36.
21. Wang HW, Lu GZ, Zhang YY, Du YW, Song LH, Li HY, Lu XY, Dong GG. Mechanical properties of phenolic foams modified by organic-inorganic nano-composite. Advanced Materials Research. 2013;753-755:604-609.
DOI: 10.4028/www.scientific.net/AMR.753-755.604
22. Gao M, Chai ZH, Wang YH, Guo CB. Phenolic foam modified with butadiene-acrylonitrile rubber as a toughening agent. Material Science and Engineering – Chen (Ed.). 2016;Chapter31:155-158.
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