

# Phenolic Foams from Wood Tar Resols

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**ABSTRACT:** This article investigates resole-type phenolic foams, in which 40% phenol was substituted with distilled oily fractions from wood tar. Different proportions of blowing agent, hexamethylenetetramine, and stabilizer, a sodium alkyl sulfate surface active agent, were used to produce a series of rigid foams, which were characterized by curing index, density and hardness. The average curing index was about 90% and densities ranged from 480 to 960 kg.m<sup>-3</sup>. A fractal dimension ( $D_f$ ) approach was used

to assess the homogeneity of pores within the foams and an average (dimensionless) value of 2.6 was found, indicating a non uniform structure. Compressive strength tests of the foams gave values above 1.0 MPa, which is higher than those for typical phenolic foams. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 923–927, 2010

**Key words:** phenolics; cellular plastics; rigid foams; fractal dimension

## INTRODUCTION

In Minas Gerais, a state in Southeastern Brazil, there are lots of iron-making industries that make use of charcoal as thermoreducing agent, hence wood tar, which is a by-product in the charcoal-making process, is generated in quite appreciable amounts. Generally wood tar is used as fuel by the industries themselves, but currently efforts have been made in order to use this by-product in applications that are less harmful to the environment and to establish the economical feasibility of this green siderurgy. Wood tar from *Eucalyptus sp.*, in particular, is rich in several phenolic compounds and it has been used to partially replace phenol to produce phenolic resins of various kinds.<sup>1–3</sup> Polyurethane in the form of flexible foams have also been prepared from biopitch (the residue from *Eucalyptus sp.* tar distillation),<sup>4</sup> but for the best of our knowledge, no phenolic resin has previously been prepared in cellular form using wood tar derivatives.

Phenolic foams from other renewable sources, such as lignin, have been prepared by Frollini and coworkers<sup>5</sup> and presented good mechanical properties such as compressive strength and hardness. Friability of these foams was low and they have been

proposed as thermal insulators, on the basis of their thermal conductivity.<sup>6</sup> Mikhanov et al. observed that water resistance of phenolic foams from lignin was improved without affecting its compressive strength.<sup>7</sup> Lignin has also been used to produce polyurethane films, foams, and composites. It was observed that, while the glass transition of these materials increased and the mechanical properties improved with higher lignin content, their thermal resistance decreased.<sup>8</sup>

Foam properties are related to its cellular structure and this can be open cell, closed cell or a mixture of both. Phenolic resin foams usually have high open cell content which leads to friability, low mechanical strength and poor insulation performance. However, for applications such as in floral arrangements, in which the foam must be entirely open cell and fully absorb water, friability and lower mechanical strength do not pose a problem. Despite the low cost of its production, phenolic foams have yet to find widespread commercial applications, but they have been successfully applied in new cultivation techniques using hydroponics<sup>9</sup> and also as alternative to tubes and baskets for producing coffee seedlings.<sup>10</sup>

In the present work resols prepared with oily fractions distilled from wood tar were used to produce phenolic foams. Hexamethylenetetramine (HMTA), which is usually employed as curing agent for phenolic resins of the novolak type, was also used as a blowing agent. During the heat treatment (resin cure) the HMTA is degraded releasing gaseous ammonia, which will blow the resin at the same time it acts as a catalyst for the cross-linking reaction. HMTA avoids the use of others traditional liquid blowing agents

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(fluorocarbons, n-pentane, etc), that might cause a negative environmental impact. Although ammonia is not an inert gas, its use is justified by the low cost of the resulting foam and the simple formulation employing inexpensive reactants, particularly the phenolic component recovered from the condensed smoke during charcoal-making activities. The effect of changing the concentration of blowing agent and surfactant on the properties of the foams was also investigated.

## EXPERIMENTAL

### Materials

Phenol, bisphenol-A, and paraformaldehyde were purchased from Synth; Ba(OH)<sub>2</sub> and HMTA were purchased from *Grupo Química*; all chemicals were commercial grade and used as received. Wood tar oil was kindly donated by Companhia Aços Especiais Itabira (ACESITA), a national steel making company, and corresponded to a light oil distilled in the range of 120–140°C. The surfactant used was a sodium lauryl ether sulfate, purchased under the trade name TEXAPON<sup>®</sup>. Nitrile rubber was kindly donated by Petroflex.

### Resol synthesis

Conductometric analysis of the wood tar oil<sup>11</sup> indicated a phenolic —OH content of 11.5%. Previous experience from our laboratory has shown that wood tar oil can replace phenol only up to 40% by mass. Thus in a typical procedure, a kettle flask provided with a thermocouple, mechanical stirrer and condenser, was charged with phenol (94.0 g, 1.0 mol), paraformaldehyde (46.0 g, 1.53 mol), wood tar oil (60.0 g, nominal phenolic content 0.4 mol) and the catalyst Ba(OH)<sub>2</sub>·8H<sub>2</sub>O (9.4 g, 0.03 mol). Following addition of water (70 mL), the mixture was kept under stirring at 80°C for 5 h and then cooled down to room temperature. The resulting product was used to formulate the foams. Viscosities of resols were within 900 and 6000 cP at 25°C.

### General procedure for foam preparation

Liquid resol prepared as above, plus bisphenol-A, and HMTA, were thoroughly mixed at room temperature before addition of the surfactant. After complete homogenisation, the mixture was poured onto a nonsticky rectangular pan and placed in oven at 70°C for 16 h. The temperature was raised to 100°C and the complete cure was attained after 48 h. After cooling down, the foam was removed from the mold to proceed characterization.

A wide range of formulations was employed, by combining the concentrations of 2.5, 5.0, and 10% of the blowing agent HMTA, and 2.0, 5.0, and 7.0% of surfactant, relative to the mass of resol used. Some of the foams also included nitrile rubber in their composition. In all formulations the amount of bisphenol-A corresponded to 1% by mass relative to resol.

### Characterization

#### Apparent density

This was obtained from the ratio of mass determined from a precision balance to volume calculated from the foam dimensions, which were measured with a vernier scale. All measurements were made at room temperature, according to ASTM-D1622.<sup>12</sup>

#### Hardness

A manual durometer TECLOK mod. GS-702N was used to measure hardness with a Shore D scale, following ASTM-D2240.<sup>13</sup> Readings were taken during 5 s at about five different locations on the sample and the results averaged.

#### Curing Indices

Samples were extracted with acetone in a soxhlet extractor and the residue was taken as the curing index, following DIN 53,700.<sup>14</sup>

#### Compressive strength

A universal testing machine KRATOS mod. 181/561 was used to evaluate compressive strengths of the foams, according to ASTM D1621.<sup>15</sup> The compression load was set to a maximum of 2000 kg and tests were run at 15 mm min<sup>-1</sup>.

#### Fractal dimension

Following an adapted procedure,<sup>16</sup> foam surfaces were coated with white paint and sandpapered, in order to give contrast between the region occupied by the cell voids and the solid region. An optical microscope LEICA mod. DNRX equipped with a camera CCD JVC mod. TK-C1 3803 with a resolution of 764 × 564 was used to picture foam surfaces and the images were processed through a analyser (LEICA QWin<sup>®</sup> v3.2) to calculate the fractal dimensions. Images with different optical magnification were obtained and the average cell size (M) was calculated as a function of measuring scale (ε), related to the corresponding magnification.

## RESULTS AND DISCUSSION

### General properties

Wood tar oil from *Eucalyptus* sp is a dark liquor with characteristic odor and a complex chemical composition. It has a high content of volatile and aromatic compounds including phenol, cresols, syringol and guayacol.<sup>17</sup> Resols prepared with this oil are also dark and when the foam is set, the characteristic odor is significantly reduced.

Table I shows some of the properties determined for the phenolic foams. A generic trend of increasing density is observed for increasing amounts of surfactant (entries 3, 6, and 9). Because the role of the surfactant is to stabilize the bubbles generated by the blowing agent, more bubbles can be stabilized when the amount of surfactant is large. As a result bubbles will not coalesce, remaining small within a given volume of the foam. This leaves less space for air being trapped within the bulk of the foam and this space is replaced by solid resin, which accounts for a higher density. The effect of increasing the amount of surfactant on the hardness of the foams is less conspicuous. However the presence of the surfactant *per se* has a favorable effect in increasing the hardness. This becomes clear by comparison of the hardness of all foams, which varies within the range 80–90, with that for a foam prepared without surfactant, which is 70 (entry 2).

Density values of foams prepared with 2.5% HMTA are higher than those for materials prepared with 5% HMTA, because in the last case a larger volume of blowing agent (ammonia) is released. This trend can be observed whatever the amount of surfactant used: 2% (entries 4 and 5), 5% (entries 6 and 7), and 7% (entries 9 and 10). On the other hand, when the HMTA content was increased to 10% (entries 5, 8, 11)

TABLE I  
Phenolic Foams Properties

Sample	Amount of surfactant (%)	Amount of HMTA (%)	Density (kg m <sup>-3</sup> )	Shore D hardness	Curing index
1	10.0	5.0	847	84 ± 1	–
2	0.0	5.0	276	70 ± 1	96.0
3	2.0	2.5	279	87 ± 1	91.7
4	2.0	5.0	221	87 ± 1	98.3
5	2.0	10.0	569	90 ± 1	91.0
6	5.0	2.5	357	88 ± 1	97.2
7	5.0	5.0	330	85 ± 1	98.5
8	5.0	10.0	584	89 ± 1	94.0
9	7.0	2.5	835	90 ± 1	96.8
10	7.0	5.0	306	88 ± 1	98.0
11	7.0	10.0	505	90 ± 1	93.4
12 <sup>a</sup>	5.0	5.0	–	83 ± 1	–
13 <sup>a</sup>	5.0	5.0	–	81 ± 1	–

<sup>a</sup> These foams included 5% nitrile rubber

the density values were higher than those obtained for foams prepared with 2.5% HMTA. A possible explanation for this behavior is that under high concentrations of HMTA, the cross-linking reaction is favored over the blowing action, so the material cures before it has time to expand.

Many substances present in the wood tar oil do not react during the polymerization, but remain in the resol, and a considerable amount of these substances are vaporized as the foaming takes place. The time and temperature used for the foaming process were sufficient to ensure a curing index over 90% for all the samples (Table I). The small amount of substances extracted with acetone when curing indices were determined probably corresponds to heavier aromatic compounds which did not react during polymerization. HMTA is well known to release ammonia when is used as curing agent for novolaks. Because of this gas releasing property it was used as the blowing agent for the foams and, although resols do not need curing agent for cross-linking, it is reasonable to assume that this blowing agent contributed to the high curing indices achieved.

### Fractal dimensions

The theory of fractals has been applied to various fields of science to describe the geometry of structures, figures and shapes resulting from a wide range of physical and chemical processes. A fractal is a fragmented geometric shape that can be dismembered into several parts, each of which can be considered, albeit roughly, a small-scale copy of the bulk.<sup>18</sup> This property, called self-similarity or self-affinity, when considered under a particular transformation scale, is common to all fractal objects.

The fractal nature of a structure is represented by its “fractal dimension” ( $D_f$ ), a dimensionless number that measures with some accuracy the dimension of complicated sets, such as fractals. The fractal dimension,  $D_f$ , also known as the Hausdorff-Besicovitch dimension, coincides with the more familiar notion of dimension in the case of well-behaved sets. For example, a straight line or an ordinary curve, such as a circle, has a Hausdorff dimension of 1. However, the fractal dimension is not always an integer: a complicated twisting line that starts to fill up the plane will have an increasing Hausdorff dimension from 1 to values closer to 2. The same approach is used to assign a fractal dimension to a plane that contorts more and more in the third dimension: its Hausdorff dimension gets closer and closer to 3.<sup>18,19</sup>

The term “fractal dimension” is, roughly speaking, the exponent ( $D_f$ ) in the expression:<sup>19</sup>

$$M = \lim_{\varepsilon \rightarrow 0} N\varepsilon^D \quad (1)$$

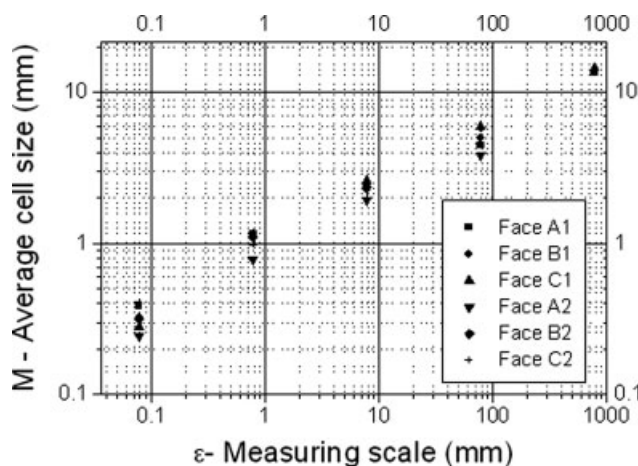


**Figure 1** Phenolic foam prepared for quantitative image analysis, showing the contrast between cell voids and solid phase.

where  $M$  is a finite measured dimension of the analyzed fractal,  $N$  is an integer,  $\varepsilon$  is a measuring scale factor and  $D_f$  the fractal dimension.

We have applied this methodology and a technique to analyze fractured surfaces in order to characterize the cell distribution within the foams. Figure 1 displays a photograph of phenolic foam prepared for quantitative image analysis, so as to present a contrast between cell voids and solid phase. This picture was studied by means of an image analyzer in order to collect data corresponding to the parameters in the above equation. For a given foam sample, data was collected from three different randomly chosen faces and a plot relating  $M$  and  $\varepsilon$  was obtained. Figure 2 shows one of such plots with logarithmic values for two different foams (samples 1 and 8). The fractal dimension for the cells can be calculated from the slopes of the lines obtained and, for a series of foams, it was found to be  $D_f = 0.395$  on average. By subtracting this value from 3.0, which represents the dimension of an Euclidean solid,<sup>19</sup> one gets  $D_f = 2.6$  as the fractal dimension of the studied foam.

The more the fractal dimension approaches 3.0, the more solid and continuous is the structure. It follows that the phenolic foams prepared are non uni-



**Figure 2** Calculation of fractal dimensions of the phenolic foams.

**TABLE II**  
Compressive Strength and Elastic Modulus of the Foams

Sample	Amount of surfactant (%)	Amount of HMTA (%)	Compressive strength (MPa)	Elastic modulus (MPa)
3	2.0	2.5	1.08	24.7
4	2.0	5.0	2.40	87.7
6	5.0	2.5	2.35	–
7	5.0	5.0	1.62	–
8	5.0	10.0	4.72	126.2
10	7.0	5.0	1.79	134.9
11	7.0	10.0	2.38	–
12	5.0	5.0	3.88	–
13	5.0	5.0	5.74	–

form, their cell structures present self-similarity and, thus, are best characterized by the fractal dimension of their cells.

### Compressive strengths of the foams

Results for compressive strength and elastic modulus of the foams are compared in Table II. Compressive strengths for all the samples tested were above 1.0 MPa, which is surprisingly high compared to traditional phenolic foams (0.14–0.62 MPa).<sup>20</sup>

Among the formulations used, a combination of 5% surfactant and 10% HMTA gave the best result for compressive strength. By incorporating an elastomer in the composition of the foam, compressive strengths can be further improved, as shown by samples 12 and 13, which were prepared with nitrile rubber. Although elastic moduli have not been determined for all the samples, an increasing trend of this mechanical parameter with increasing surfactant content can be deduced. It is possible to infer that the best combinations of surfactant and blowing agent for these phenolic foams lie around 5–7% for the former and 5–10% for the latter.

### CONCLUSIONS

It was demonstrated that phenolic foams can be prepared from resols containing oily fractions of *Eucalyptus sp.* tar. This by-product from charcoal-making activities can be incorporated in resol formulations replacing up to 40% mass of pure phenol, which might represent a substantial reduction in the cost of phenolic resins. HMTA, which is widely used as curing agent for novolaks, has performed quite well as blowing agent in the foaming process. Concentration of blowing agent and surfactant affected the densities of the foams in such a way that increasing amounts of surfactant reflected in higher densities. This was explained on the basis of bubbles being stabilized more effectively when a greater proportion of surfactant is present. Hardness of the foams

was also augmented by the presence of surfactant. Compressive strength tests indicated that phenolic foams reported here are potential structural foams. A combination of surfactant and blowing agent in the range 5–7% and 5–10%, respectively, has been suggested as ideal in order to achieve better mechanical properties and the use of nitrile rubber increases the compressive strength. A thorough investigation of potential applications for these foams is currently underway and shall be reported in a future publication.

## References

1. Dos Santos, C. G.; Laranjeira, D. A.; Carazza, F. *Quim Nova* 1988, 11, 284.
2. Pasa, V. M. D.; Assis, R. S.; Bruns, R. E.; Dos Santos, C. G. *Bull Chem Soc Japan* 2008, 81, 1528.
3. Prauchner, M. J.; Pasa, V. M. D.; Otani, C.; Otani, S.; de Menezes, S. C. *J Appl Polym Sci* 2004, 91, 1604.
4. Araújo, R. C. S.; Melo, B. N.; Pasa, V. M. D. *Eur Polym J* 2005, 41, 1420.
5. Carvalho, G.; Frollini, E. *Polimeros: Ciencia e Tecnologia* 1999, 9, 66.
6. Carvalho, G.; Frollini, E. *J Macromol Sci Pure Appl Chem* 2002, 39, 643.
7. Mikhanov, S. A.; Golubev, V. M.; Bilimova, E. S. *Plasticheskie Massy* 1986, 9, 60.
8. Hatakeyama, H.; Hirose, S.; Nakamura, K.; Hatakeyama, T. *Cellulosics: Chemical, Biochemical and Material Aspects*; Kennedy, J. F., Phillips, G. O., Williams, P. A., Eds.; Ellis Horwood: London, 1993; p 525.
9. <http://www.agr.unicamp.br/publicacoes>. Accessed on February, 2006.
10. <http://www.coopemar.com.br/cf>. Journal online Dec/2000 Accessed on February, 2006.
11. Sarkanen, K. V.; Herget, H. L. *Lignins: Occurrence, Formation, Structure and Reactions*, Sarkanen, K. V., Ludwig, C. H., Eds.; Wiley-Interscience: New York, 1971.
12. ASTM-D1622, Standard Test Method for Apparent Density of Rigid Cellular Plastics.
13. ASTM-D2240, Standard Test Method for Rubber Property – Durometer Hardness.
14. DIN 53700, Determination of Acetone Soluble Matter in molded Polymers.
15. ASTM-D1621, Standard Test Method for Compressive Properties of Rigid Cellular Plastics.
16. Hsiung, J. S.; Chou, Y. T. *J Mat Sci* 1998, 33, 2949.
17. Chen, C. A.; Pakdel, H.; Roy, C. *Biomass and Bioenergy* 1997, 13, 25.
18. Mandelbrot, B. B. *The Fractal Geometry of Nature*; Freeman: New York, 1983.
19. Rasband, S. N. *Chaotic Dynamics of Nonlinear Systems*; Wiley-Interscience: New York, 1990; p 71.
20. Such, K. W.; Webb, D. D. *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley: New York, 1989; Vol. 3. p 5.