LIGNIN IN PHENOLIC CLOSED CELL FOAMS: THERMAL STABILITY AND APPARENT DENSITY

Gil de Carvalho[ab]; Elisabete Frollini[a]

[a] Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos, SP, Brazil [b] Instituto Politécnico, Universidade Estadual do Rio de Janeiro, Nova Friburgo, RJ, Brazil

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Gil de Carvalho* and Elisabete Frollini[†]

Instituto de Química de São Carlos, Universidade de São Paulo, Cx. P. 780, CEP 13560 970, São Carlos, SP, Brazil

ABSTRACT

Lignin, extracted from sugarcane bagasse, was used as a partial phenol substitute in phenolic closed cell foams. The thermal stability of phenolic and lignophenolic foams were studied using thermogravimetric (TG) and differential scanning calorimetry (DSC) techniques, under air and nitrogen atmospheres. The results of apparent densities (Dapp) are also reported for both foams. The thermal analyses data showed that the decomposition depends on the atmosphere, that is, this process is not only a thermal one and, that it is feasible to replace part of the phenol by lignin in closed cell foams. Regarding the apparent density, that replacement was extremely advantageous because the Dapp value obtained placed the lignophenolic foam in the structural foam class.

Key Words: Lignin; Phenolic foams; Lignophenolic foams; Thermal stability; Closed cell foam; Thermogravimetry; Differential scanning calorimetry; Apparent density

*Current address: Instituto Politécnico, Universidade Estadual do Rio de Janeiro, Cx. P. 97282, CEP 28601 970, Nova Friburgo, RJ, Brazil.
[†]Corresponding author. Fax: +55 16 273 9952; E-mail: elisabete@iqsc.sc.usp.br

INTRODUCTION

Foams can be defined as a plastic whose apparent density suffered a significant reduction due to the presence of numerous cells distributed along their bulk. The foam is a two-phase system, one solid and one gaseous, in which the continuous solid phase is a plastic and the gaseous phase is distributed in voids that form the cells. These cells can be interconnected (open cells) or the distribution of the cells can occur in a discrete form, being the gaseous phase of each cell totally independent from the other (*closed cells*).[1]

The apparent foam density depends on the fraction of the total volume occupied for the polymer that composes its structure. The structural foam consists of a nucleus of reduced apparent density, formed by closed cells, coated by a fine layer of the same polymer (the so-called skin), combining in this way, thermal insulation with mechanical strength. The term structural foam does not have a precise definition, but it can be considered that they are rigid foams, having a density superior to $320 \, Kg/m^3$.[2]

In thermoset foams, the macromolecules are crosslinked during the expansion process, being that the synchronism of the crosslinking chemical process with the expansion is one of the biggest difficulties in foam production. Foaming is formed by the volatilization of the expansion agent (for example, a liquid of low boiling point), which in turn occurs due to the heat produced by the pre-polymer cure. The expansion can also be a result from the action of chemical agents, which are solids that decompose themselves at high temperature, releasing a gas component.[3,4] Besides, the expansion agents can be formed as a by-product of the reaction.[5]

From phenolics (obtained by polycondensation under alkaline catalysis), the foam is produced through an acid catalyzed cure reaction. The vaporization of the expansion agent, normally a halogenated hydrocarbon added to the pre-polymer, occurs due to the heat liberated by the crosslink reaction. The presence of a surfactant, which emulsifies the expansion agent and stabilizes the forming foam, is necessary. The cure is done in the presence of an aromatic acid, that, if chosen conveniently, besides acting as an accelerator of the reaction, will be incorporated into the chains, acting also as a crosslink agent. The cure can occur by thermal treatment at a temperature of 70°C, or higher in some cases.[4]

The phenolic foams were developed in the 40s, but the technology to obtain closed cells is more recent, because initially the phenolic foams were just open cells type. The foams with closed cells retain the expansion agent that, by being a gas of low thermal conductivity, results in a material that can be used for thermal insulation.[4,5]

Lignin, a complex macromolecule present in many vegetables, is constituted of aromatic rings of a phenolic type, which turns it into a potential phenol substitute in phenolic resins,[6−10] with the advantage that this mac-

romolecule is obtained from renewable raw material. Lignin can be found in many plants, but its constitution is not the same in all of them. Therefore, lignin shouldn't be considered like a chemical substance, but as a class of correlated materials, which can be divided into two classes: guaiacyl- and siringyl-lignin. Guaiacyl lignin contains mainly guaiacyl units, while guaiacyl-siringyl contains almost the same proportion of guaiacyl and siringyl units. Both kinds of lignin also have smaller proportions of p-hydroxy phenyl units (Fig. 1).[11]

Sugar cane belongs to the class of annual plants and, in this case, the lignin has a higher proportion of aromatic rings of p-hydroxyphenyl type (Fig. 1) than the other plants. In these units, the 3 and 5 aromatic ring positions are free, which turns these rings more reactive, making the sugarcane bagasse lignin more suitable to be used as a partial phenol substitute in phenolic resins.[6–10]

The objective of this project is to acquire phenol and lignophenolics closed cell foams, looking for materials that behave as thermal insulators. In the present work, the thermal stability under different atmosphere and apparent densities of these foams are evaluated. The results related to other mechanical properties and to the thermal conductivity of these foams will soon be published.

EXPERIMENTAL

Pre-polymer Synthesis

Phenolic Pre-polymer (Resol)

Phenolic pre-polymer (resol) was synthesized using phenol, formaldehyde (37% aqueous solution) and potassium hydroxide (100, 138 and 6 g, respectively) with mechanical stirring under reflux (70°C, 30 min). The solution was then cooled to room temperature and HCl was added until neutralization, the water eliminated under reduced pressure.
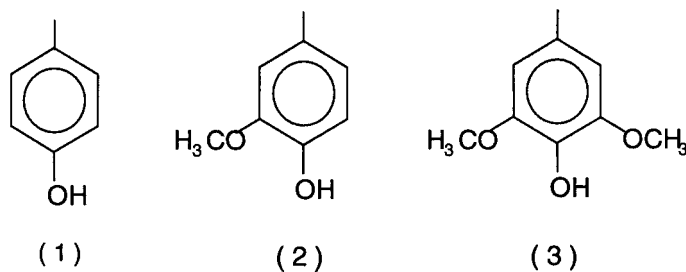

Figure 1. Basic units in lignin: p-hydroxyphenil (1), guaiacyl (2), and siringyl (3).

Lignophenolic Pre-polymer

A pre-polymer was also synthesized, partially replacing the phenol (25% w/w) by lignin (*organosolv* lignin kindly given by Dedini-Piracicaba/SP/Brazil; Mw = 2600 g/mol; Mw/Mn = 1.6). Formaldehyde (50 g) was added to a KOH aqueous solution (2 g/100 mL) of lignin (25 g), keeping the solution under reflux (70°C) and mechanical stirring for 70 min.

The methylol group (-CH$_2$OH) was inserted in the phenolic rings of lignin. After that, phenol (75 g), KOH (4 g) and formaldehyde (112 g) were added to the "methylolated" lignin following a procedure similar to the one described above for the phenolic pre-polymer, using 45 min as a reaction time, instead of 30 min, due to the lower reactivity of lignin phenolic ring, when compared to the phenol aromatic ring.

Foam Molding

Phenolic Foam

The resol phenolic pre-polymer was mixed under mechanical stirring at room temperature, with resorcinol, surfactant (DABCO DC 5604), an expansion agent (trichloro-trifluoro-methane was used, due to the possibility of comparing the thermal conductivity data obtained with that available in the literature), and an aqueous solution of phenolsulphonic acid (100:1:2:10: 10 w/w, respectively). The mixture was poured into a metallic mold (20,050 × 25 mm), previously covered with a demolding agent (*carnauba* wax). The cure was then carried out at 70°C for 12 hr.

Lignophenolic Foam

The lignophenolic pre-polymer was mixed under mechanical stirring at room temperature with resorcinol, surfactant (DABCO DC 5604), an expansion agent (trichloro-trifluoro-methane), and an aqueous solution of phenolsulphonic acid (100:10:1, 5:20:40 w/w, respectively). The composition of the mixture was changed, related to the one used for phenolic foam, due to the lower reactivity of lignophenolic pre-polymer. The cure step followed the same procedure described above for phenolic foam.

Measurements

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry measurements were carried out using TA instruments equipment (Model DSC 2010). Samples of approximately

10 mg were placed in aluminum pans and analyzed using a dynamic temperature scan from 25 to 550°C with a heating rate of 10°C/min. Two sets of experiments were carried out: a) under nitrogen atmosphere (80 mL/min); and b) under air atmosphere (80 mL/min).

Thermogravimetric Analyses (TG)

Thermogravimetric analyses were carried out using TA Instruments equipment (Model TGA 2050). Samples of approximately 10 mg were placed in aluminum pans and heated from 25 to 600°C at 10°C/min. Two sets of experiments were carried out: a) under nitrogen atmosphere (80 mL/min); and b) under air atmosphere (80 mL/min).

Apparent Density

The apparent density was performed according to ASTM-D-1622.[12] Samples of phenolic and lignophenolic foam were analyzed and also a polyurethane foam, which was considered as a reference sample, aiming to compare its property with those of phenolic and lignophenolic foams.

RESULTS AND DISCUSSION

Thermogravimetry (TG)

Different samples of foams were submitted for thermogravimetric analysis, being those denominated as described in Table 1.

Tables 2 and 3 show values of weight loss in different temperature ranges obtained directly from the thermogravimetric (TG) curves (curves not shown), under air and nitrogen atmosphere, respectively.

For the discussion of results below, four steps of weight loss will be considered:

Table 1. Description of the Lignophenolic and Phenolic Samples Submitted to Thermogravimetric Analysis

Sample	Foam Type	Properties
LP-1	Lignophenolic	Foam surface skin
LP-2	Lignophenolic	Foam wall
P-1	Phenolic	Edge of the foam
P-2	Phenolic	Foam wall

Table 2. Weight Loss of Lignophenolic and Phenolic Samples (%) Obtained from TG Curves (Air Atmosphere, 80 mL/min; Heating Rate of 10°C/min)

Sample	Temperature Range [°C]				Residue
	25−100	100−300	300−400	>400	
LP-1	11	10	16	60	3
LP-2	17	8	17	55	3
P-1	2	10	7	77	4
P-2	2	8	8	80	2

First step − From ambient temperature up to 100°C − there is a weight loss more accentuated for the lignophenolic foam, which can be attributed to the higher amount of aqueous solution of phenolsulphonic acid used for that foam, when compared to the phenolic foam, which leads to a higher amount of water that vaporizes in this interval.

Second step − 100−300°C − It can be characterized as the interval of thermal stability of the polymer. Comparing the thermal behavior of the foam with that of the resins described in the literature,[13] where it is affirmed that the amount of gas components volatilized in this step is relatively small. In the case in study, a higher loss of mass is observed. In this temperature interval, the weight loss is attributed to volatilization of monomers that did not react, which were occluded during the cure.[13] Because the pre-polymer used for the production of foam has a molar mass smaller than the pre-polymers used in other applications, the amount of occluded monomers probably were higher and also then, the amount of volatile released.

Third step − between 300−400°C − The weight loss that occurs in this stage is attributed to the beginning of the thermal decomposition, and the behavior is similar for both foams.

Table 3. Weight Loss of Lignophenolic and Phenolic Samples (%) Obtained from TG Curves (N_2 Atmosphere, 80 mL/min; Heating Rate of 10°C/min)

| Samples	Temperature Range [°C]				Residual
	25−100	100−300	300−400	>400	
LP-1	12	12	14	10	52
LP-2	17	8	12	10	53
P-1	4	8	6	10	72
P-2	4	6	6	12	72

The fourth step encompasses temperatures higher than 400°C until the formation of residue, and it corresponds to the main thermal-decomposition step, where the chain linkages are randomly broken. However, the process is not characterized as a depolymerization. The rate of decomposition reaction reaches the upper limit at this step and several decomposition products are released (water, carbon monoxide, carbon dioxide, methane, phenol, cresol, and xylenol), which were formed due to the chain linkages and/or due to the interactions with the gaseous atmosphere presents.[13]

It must be emphasized that there is no significant dependence in the thermal behavior of foams (LP-1 and LP-2; P-1 and P-2) relating to the region where the samples were withdrawn, which can be taken as an indication that the expansion occurred in a homogeneous way for both the phenolic and lignophenolic foams.

At high temperatures (400−500°C), under inert atmosphere, the oxidation can involve the methylenic bridge that connects the aromatic rings. These reactions can, for instance, involve a homolytic break of the connections between the ring and methylenic bridge, and between the ring and phenolic hydroxyl, both generating radicals (Eqs. 1 and 2), as is proposed in the literature.[14,15]


$$(1)$$

$$(2)$$
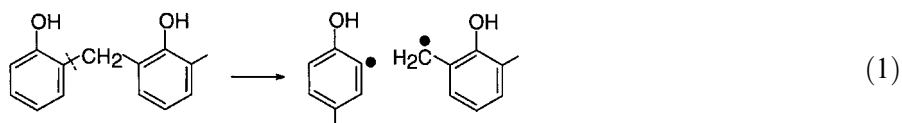
The reactions between these highly reactive species can lead, besides other products,[14−16] to:

$$(3)$$
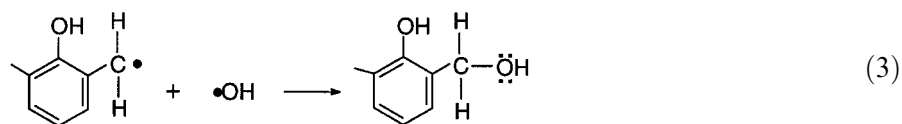
The further oxidation of this group leads in a first stage to the aldehyde group, which easily oxidizes to carboxylic groups, whose decarboxylation leads to a CO_2 release (Eq. 4):

$$(4)$$
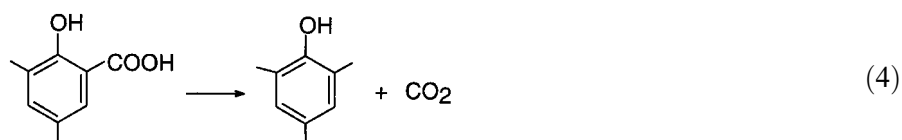
In the presence of air, oxygen is the oxidant agent, leads to the formation of carbonyls groups (Eq. 5) and, in this case, the oxidation can occur at lower temperatures (near $300°C$).

$$\text{(5)}$$
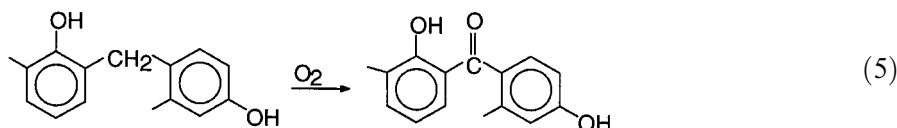
These carbonylated compounds formed at higher temperatures can generate carboxylic acids and then carbonic gas.[14−16]

In the present work, the thermal-decomposition mechanism of the foam using, for instance, mass spectrometry or spectroscopic methods, was not investigated. It is assumed that the mechanism is similar to the above described, because the results are compatible with this assumption. Then, it is considered that the vaporization of volatile products generated in these reactions previously mentioned, leads to the weight loss observed in the fourth step.[16]

Even though the TG curves that rendered the data described in the above tables showed a similar behavior, the samples related to phenolic foams, P-1 and P-2, presented a lower weight loss, also in the third and fourth steps, when compared to those of lignophenolic foams (samples LP-1 and LP-2). Relating to its chemical structure, lignin can be seen as a phenyl-propane based polyether[19] and probably the breakage of these and other linkages present in lignin moiety of the structure of the foam, leads to the higher weight loss of lignophenolic type foams.

Figures 2 and 3 show the behavior of the bulk of foams under air and N_2 atmosphere respectively. The biggest weight loss of LP (lignophenolic sample), which is observed either in the presence of air as in N_2, can be attributed to a higher amount of phenolsulphonic aqueous solution used in that lignophenolic foam, and also due to the presence of lignin, as was mentioned above.

Comparing TG curves obtained in air and N_2 atmospheres (Fig. 4), it can be observed that the thermal behavior is very similar for the lignophenolic, as well as for the phenolic foam, up to about $400°C$ in both atmospheres. However, above $400°C$, the thermal process is extremely dependent on the atmosphere, indicating that the decomposition is not only a thermal process.

Differential Scanning Calorimetry (DSC)

Figure 5 shows the DSC curves for phenolic and lignophenolic foams.

In accordance with what was observed in the thermogravimetric analysis, only for lignophenolic foam (LP) near $100°C$, an endothermic peak is observed as a consequence of the high amount of phenolsulfonic acid aqueous solution used in the preparation of that foam.
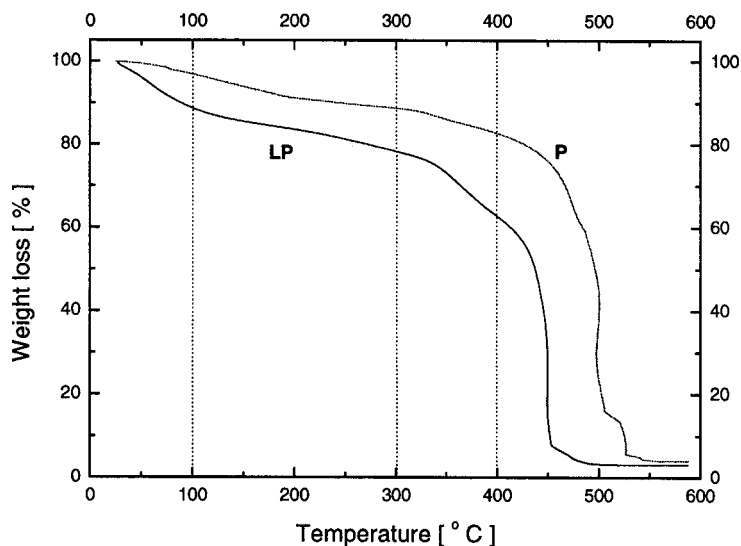
Figure 2. TG curves (air atmosphere, 80 mL/min; heating rate of 10°C/min) of: LP-ligno-phenolic foam, P-phenolic foam.

No heat flux variation occurs up to 300°C, which indicates that a residual cure did not occur during the scanning. The thermal cure of the phenolic resins takes place normally at temperatures higher than 70°C. It was observed that the addition of phenolsulfonic acid lead to a completely cured
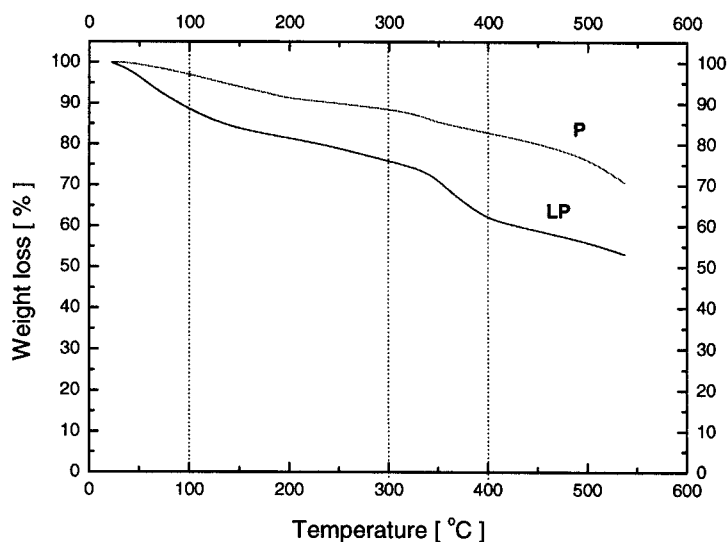

Figure 3. TG curves (N_2 atmosphere, 80 mL/min; heating rate of 10°C/min) of: LP-ligno-phenolic foam, P-phenolic foam.
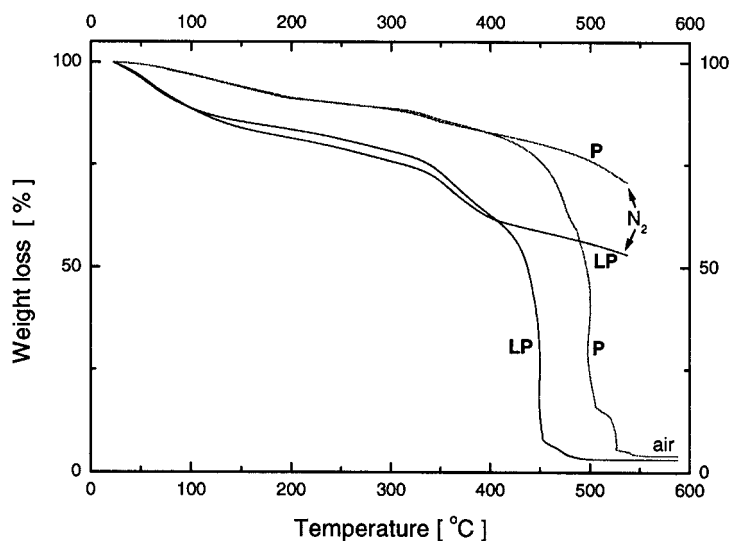
Figure 4. TG curves (air and N$_2$ atmosphere, 80 mL/min; heating rate of 10°C/min) of LP-lignophenolic foam, P-phenolic foam.

foam at 70°C. This result confirms the role of the acid as a cure accelerator, because when the same step occurs only as a thermal process, in the absence of that acid, it is necessary to use time interval and temperatures higher than those used in this work.[17]
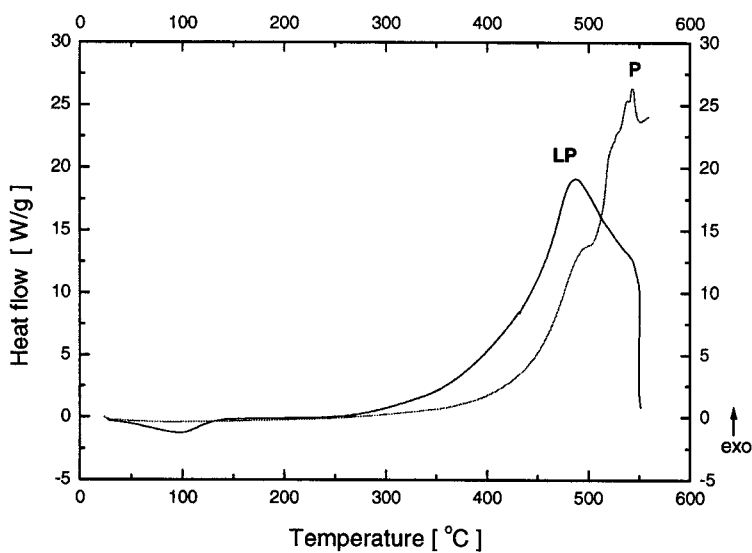

Figure 5. DSC curves (air atmosphere, 80 mL/min; heating rate of 10°C/min) of: LP-lignophenolic foam, P-phenolic foam.

If one considers the applications of phenolic resins in closed cell foams, as is the objective of the present work, then, in that case, it is interesting that the cure occurs at lower temperatures than those of phenolic resins used in other applications. High temperatures can lead to an excessive volatilization of the expansion agent, which is one of the fundamental components in the foam formulation. In this case, this factor is more important than the resulting completely cured foam.

It must be pointed out that the absence of variation in the heat flux near 300°C proves that the phenolsulfonic acid was incorporated into the polymeric network, since the presence of free phenolsulfonic acid would have rendered a peak around 270°C, which is the temperature of its decomposition.[18]

The main step of decomposition occurs from 300°C, as is indicated by the outset of an exothermic peak, which in turn agrees with that observed in thermogravimetric analysis. Figure 5 shows that the lignophenolic foam decomposes at lower temperatures than phenolic foam, as observed also in the thermogravimetric analysis (Fig. 4). Such difference in behavior is not relevant in this case, once the service temperature of a thermal insulator material is lower than 300°C.

The DSC curves shown in Fig. 6 are representative for both samples, lignophenolic and phenolic foams, once the obtained curves are similar (phenolic curves not shown), with the exception of the endothermic peak at 100°C, because the phenolic foam barely shows a loss of water, as observed in the thermogravimetric analysis (Fig. 4).

Comparing the curves obtained in air and in N_2 (Fig. 6), a different behavior can be noticed. Under N_2 atmosphere there is no reaction up to
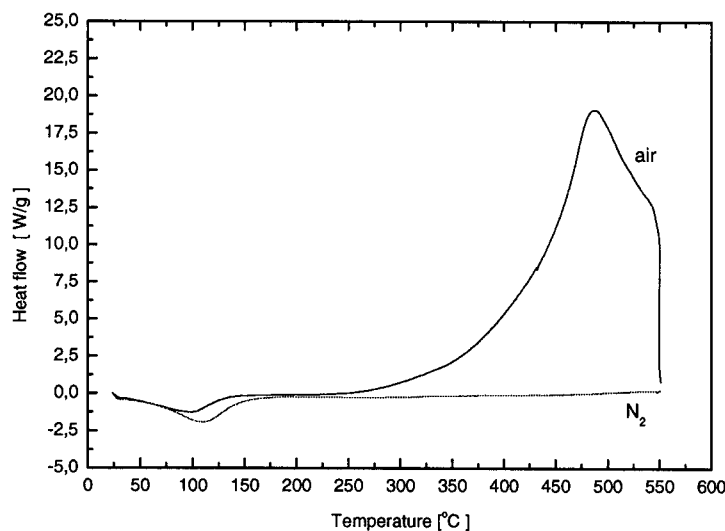

Figure 6. DSC curves (air and N_2 atmospheres, 80 mL/min; heating rate of 10°C/min) of: LP-lignophenolic foam.

550°C, but, under air atmosphere, the DSC curve shows an exothermic peak, which can be linked to a decomposition step, confirming that the foam decomposition is not just a thermal process.

Apparent Density (Dapp)

The values of apparent densities (Dapp) obtained for phenolic and lignophenolic foams are shown in Table 4.

The apparent density is a parameter that characterizes the ratio of solid/gas content in a material. For polymeric foams, it is a fundamental parameter, due to its influence in mechanical, thermophysical and electric properties.

Foams with apparent density higher than $320 \, kg/m^3$ are classified as structural foams, which are very important from the point of view of application.[20] The value of density obtained for lignophenolic foam (Dapp $= 450 \, kg/m^3$) inserts this material in the structural foams class, while phenolic foam does not show the same characteristic (Dapp $= 120 \, kg/m^3$). Therefore, regarding this mechanical property, the partial substitution of phenol by lignin was extremely advantageous.

CONCLUSION

Considering the thermal analyses data, it can be inferred that the partial substitution of phenol by lignin does not influence the thermal stability of the foam to a point of compromising its application. Furthermore, experiments can be done looking for the possibility to control the heat liberation, in order to use a more concentrated phenolsulfonic acid aqueous solution, which in turn will decrease the amount of vaporized water.

Concerning the results of apparent density, that difference between the values obtained for phenolic and lignophenolic foams is probably related to: a) the higher extension of crosslinkage in lignophenolic than in phenolic foam, and b) the higher content of closed cells in lignophenolic foam than in phenolic, as proved by other evaluated properties (not shown in the present text, to be published soon).

Table 4. Apparent Densities (Dapp) of Foams and Standard Deviation Values (s)

Samples	Dapp (kg/m^3)	s (%)
Polyurethane foam	28	2
Phenolic foam	120	3
Lignophenolic foam	450	3

The set of results described in the present work indicated that it is feasible the partial substitution of phenol by lignin in thermal insulating foams. Furthermore, this substitution can lead to better mechanical properties; for instance, apparent density.

ACKNOWLEDGMENT

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