



## Polybenzoxazine foams: Modeling mechanical properties

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# Polybenzoxazine foams: Modeling mechanical properties

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## Abstract

Flame retardant polybenzoxazine foams containing 1% P were prepared from diphenolic acid-based benzoxazine (DPA-Bz) and 9,10-dihydro-9-oxa-10-(1-hydroxy-1-methylethyl)phosphaphenanthrene-10-oxide (DOPO-2Me). Statistical predictive models were developed to determine the influence of the foaming time ( $t_f$ ) and foaming temperature ( $T_f$ ) on the density, compressive modulus and compressive strength of the foams. Results showed that the density of the foams exhibited great dependence on  $t_f$ , whereas both compressive properties were more dependent on  $T_f$  and  $t_f$ . Additionally, the flammability of the foams was also characterized by the limiting oxygen index (LOI). The presence of DOPO-2Me greatly improved the flame retardancy of the resulting foams.

## Keywords

Modeling and simulation, mechanical properties, polybenzoxazines, self-foaming, statistical analysis

## Introduction

Conventional phenolics are crosslinked products of low molecular weight precursors, typically formed through a condensation reaction between phenols and aldehydes. They are widely produced industrially due to the versatility of their structures and the fact that they display desirable properties. However, there are some drawbacks associated with these materials such as poor toughness properties, poor shelf life, and production of

byproducts during their process of polymerization that requires, in many cases, the use of a strong acid or base catalyst to cure.<sup>1</sup> In the search for higher performance replacements for phenolic resins many materials have received attention, and published reports of the preparation of aromatic oxazines, or benzoxazines, date back some 60 years.<sup>2</sup> Although commercial exploitation of the corresponding polymers has only come about relatively recently, they are now receiving a great deal of academic and industrial interest.<sup>3</sup> Polybenzoxazines have many advantageous characteristics compared with the traditional phenolic resins, such as high thermal stability, excellent mechanical properties and easy processability.

Over the last years, rigid polymer foams are gaining interest as core materials for sandwich structures in aerospace, naval and automotive and other commercial applications due to their higher energy absorption capabilities, especially in the event of impact loading. Among them, phenolic foams exhibit low thermal conductivity, exceptional fire-resistant properties, high thermal stability over a broad range of temperatures and low cost.<sup>4</sup> However, structural applications of phenolic foams have been limited due to the friable and brittle nature of these foams. Regarding to the study of polybenzoxazine foams, limited work has been done, most referred to bisphenol A-based benzoxazine.<sup>5-8</sup> It is recently reported a rigid phenolic foam from a renewable diphenolic acid-based benzoxazine<sup>9</sup> and also their phosphorus-containing flame retardant counterparts.<sup>10</sup> In this last work, it was studied the effect of curing conditions and type of phosphorus additive on density, cellular structure, thermal stability and flammability of the foams.

The structural response of polymeric foams strongly depends on the foam density, microstructure, such as cell size, shape, type (open or closed) and solid polymer properties.<sup>11</sup> So, it is a challenge to model the foam properties in function of the variables involved in the foaming process.

Different analytical tools have been employed to predict the elastic behavior of foams as a function of cell irregularity and relative density. An alternative approach to the mechanical modeling of foams involves the use of statistical methods. Statistical approaches greatly reduce the number of experimental iterations required when comparing to other modeling approaches while simultaneously yielding a wealth of information about multiple, interacting variables which influence the system. Some works have reported the use of statistical approaches to analyze the influence of material or formulation variables on the mechanical properties of reinforced epoxy foams<sup>12</sup> or phenolic foams.<sup>13-15</sup>

The aim of the present work is to develop a statistical model describing the density ( $\rho$ ), compressive modulus ( $E$ ) and compressive strength ( $\sigma$ ) of the previously reported phosphorus flame retardant polybenzoxazine foam,<sup>10</sup> in terms of the foaming process variables: temperature and time. Glass transition temperature ( $T_g$ ) and limiting oxygen index (LOI) values of the foam samples have also been considered. An experimental design has been used to establish the simplest model that fit to the experimental data, following the response surface methodology (RSM).<sup>16</sup>

**Experimental**

*Materials*

The following chemicals were obtained from the sources indicated and used as received: paraformaldehyde (Probus) and 4,4'-bis(4-hydroxyphenyl)pentanoic acid (DPA) (Aldrich). 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) (Aismalibar S.A) was previously dehydrated at 0.1 mbar for 3 h/130 °C, 1 h/145 °C and 1h/160 °C. 1,3,5-Triphenylhexahydro-1,3,5-triazine, 9,10-dihydro-9-oxa-10-(1-hydroxy-1-methylethyl) phosphaphenanthrene-10-oxide (DOPO-2Me) and 4,4'-bis-[6-(3-phenyl-3,4-dihydro-2H-1,3-benzoxazine)]pentanoic acid (DPA-Bz) (Figure 1) were synthesized according to reported procedures.<sup>10,17</sup>

*Crosslinking reaction*

Precursor solution was prepared by dissolving 16.9 g of DPA-Bz and 3.1 g of DOPO-2Me in dichloromethane. Solvent was removed from the solution by evaporation at 45 °C for 60 h and then at 140 °C for 10 min at 0.1 mbar. In order to obtain a prepolymer sample, the mixture was transferred to a stainless steel mold (cavities dimensions: 1.5 cm x 1.5 cm x 7 cm) and compressed under a pressure of 135 bar using a hot press for 4 h at 140 °C. The amount of DOPO-2Me used was 15.6 wt.% of the total mixture weight which corresponds to a 1% phosphorus content.

*Foaming process*

A rigid foam was obtained by heating in a conventional oven the prepared prepolymer from 30 °C up to selected foaming temperature and time (Table 1) at a heating rate of 2 °C/min. Eleven foams were prepared by varying the foaming conditions. After the foaming process, the sample was allowed to cool slowly to room temperature. The surface was peeled off before analysis.

## Instrumentation

T<sub>g</sub> of precursors and foamed materials was determined using a Mettler DSC821e thermal analyzer at a scanning rate of 20 °C/min with N<sub>2</sub> as a purge gas (100 ml/min). Thermal stability study was performed on a Mettler TGA/SDTA851e/LF/1100 using N<sub>2</sub> as a purge gas at a heating rate of 10 °C/min

Polymer foam density was calculated by dividing the weight by the measured volume of rectangular shaped specimens of 1 cm x 2 cm x 2 cm. The density value was determined from the average of at least three measurements using different samples.

Mechanical properties were determined at 25 °C using an Instron machine 3366 with a 100 N load cell. Rectangular samples with an average thickness of 1 cm and a cross-section area of ca. 4 cm<sup>2</sup> were compressed between two parallel steel plates using a crosshead speed of 1 cm/min. The compressive properties were determined from stress-strain curves of the average of at least three measurements using different samples.

LOI measurements were performed using a Stanton Redcroft FTA flammability unit provided with an Oxygen Analyzer. Three foamed samples of 1 cm x 1 cm x 10 cm were tested.

## Model experimental set-up and procedure

The foaming process was studied in the experimental domain defined by the following ranges: from 170 °C to 210 °C for temperature, and from 1.5 h to 2.5 h for time. In terms of the experimental design, the highest and lowest values of each variable are respectively codified as (+1) and (-1).

The response surface methodology (RSM) was used to find the simplest model that allows predicting the response ( $y$ ): density ( $\rho$ ), compressive modulus ( $E$ ) and compressive strength ( $\sigma$ ), in function of temperature and time.

The first model postulate was given by Equation (1):

$$y = b_0 + b_1 x_1 + b_2 x_2 + b_{12} x_1 x_2 \quad (1)$$

where,  $b_i$  are the linear coefficients which describe the sensitivity of  $y$  response to the variations in the process variables ( $x_1$  and  $x_2$  refer to codified variables: temperature and time, respectively), and  $b_{12}$  is the crossproduct coefficient which enable to establish the first-order response surface.

Four experiments (1-4) in the conditions associated to a  $2^2$  factorial design were performed to calculate the coefficients. Also, three additional experiments (5-7) were carried out, in the conditions of midpoint of the range studied (Table 1), to evaluate the significance of the coefficients in the model, employing an ANOVA test.<sup>18</sup>

To evaluate if this model fits to the experimental data, the sum of squares for pure quadratic curvature ( $SS_{\text{pure quadratic}}$ ) are calculated as follows: (Equation 2)

$$SS_{\text{pure quadratic}} = \frac{n_F n_C (\overline{Y_F} - \overline{Y_C})^2}{n_F + n_C} \tag{2}$$

where  $\overline{Y_F}$  is the average of the response of the experiments 1-4 and  $\overline{Y_C}$  is the average of the responses of the experiments 5-7,  $n_F=4$  is the number of points in the factorial design and  $n_C=3$  is the number of replicates at the midpoint. The sum of squares for pure quadratic curvature ( $SS_{\text{pure quadratic}}$ ) was compared with the  $SS_{\text{residual}}$  obtained with the replicates of the midpoint by means of an F-test.<sup>16</sup> There is no quadratic curvature when both values are statistically comparable. If this does not occur, a second-order model was postulated by means of Equation 3:

$$y = b_0 + b_1 \cdot x_1 + b_2 \cdot x_2 + b_{12} \cdot x_1 x_2 + b_{11} \cdot x_1^2 + b_{22} \cdot x_2^2 \tag{3}$$

where  $b_{11}$  and  $b_{22}$  are the new coefficients that correspond to the quadratic terms that describe the curvature.

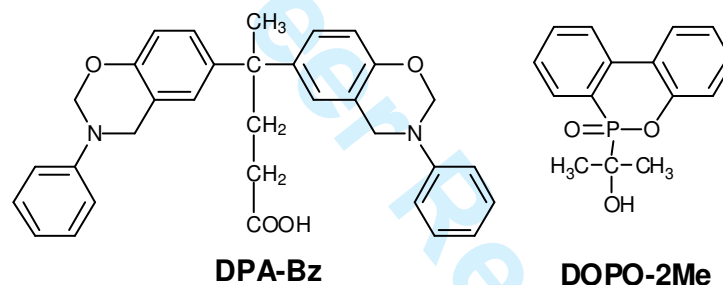
A common strategy for obtaining second-order response surfaces is to use a central composite design (CCD). This design locates the axial points on the centres of the faces of the previous full factorial design  $2^2$ . In this work, four CCD (11 runs:  $2^2 + 3$  centre points + 4 star points) were performed to calculate the coefficients between a foam property and temperature and time. The experimental conditions that correspond to the CCD are collected in Table 4. Data processing was performed using statistical software/statgraphics.

**Results and discussion**

*Preparation of the flame retardant foams*

The benzoxazine DPA-Bz (Figure 1) was obtained from the non-toxic renewable diphenolic acid (DPA) which contains a carboxylic group capable to thermal decarboxilation. Thermal curing of DPA-Bz under pressure leads to a crosslinked

system with high crosslinking degree due to the additional esterification reactions between the carboxylic groups and the phenolic OHs, formed during the ring opening of the oxazine ring. Additionally, released CO<sub>2</sub> acts “in situ” as foaming agent leading to rigid polybenzoxazine foams.<sup>9</sup> DOPO-2Me (Figure 1) was prepared as previously described from DOPO. DOPO-2Me has been proved as an effective phosphorus additive of DPA-Bz producing homogeneous mixtures and foams with relatively uniform closed cell structure and spheroid geometry.<sup>10</sup> Density, cell size and cell size distribution were found to strongly depend on the prepolymer preparation and the foaming process conditions. These structural parameters are governed by the foaming technology in processing and play an important role in determining the properties, which, in turn, dictate de foam’s possible application.<sup>19</sup> As the most applications of rigid polymer foams are structural, the mechanical properties are a crucial parameter. So, establishing statistical models which allow accurately predict the final mechanical properties as a function of the foaming conditions is still a challenge nowadays.



**Figure 1.** Chemical structures of DPA-Bz and DOPO-2Me

Prepolymer was prepared by mixing appropriate amounts of DPA-Bz and DOPO-2Me to yield mixtures with 1% phosphorus content, and heating at 140 °C for 4 h using a hot press. In this way, a rigid material with a T<sub>g</sub> of 100 °C was obtained. Samples of this prepolymer were self-foamed, by heating at different preset temperatures (170 °C, 190 °C and 210 °C) and times (1.5, 2.0 and 2.5 h) following the conditions associated to a 2<sup>2</sup> factorial design. Temperature and time ranges were selected according to previous studies,<sup>9</sup> as well as to the results of dynamic and isothermal TGA experiments of the prepolymer material.

### *Foam density model*

Table 1 shows the measured density values for the four foamed samples (runs 1-4) obtained in the conditions designed according to the 2<sup>2</sup> experimental design. As can be

observed the foam density decreases as the temperature increases, independently of the considered time. Moreover, a slight diminution occurs when time is increased. These variations are similar to those observed for the three replicates, done in the conditions of the midpoint of the experimental domain (runs 5-7), which can be considered representative of the experimental error. So, it appears to be that time, as foaming variable, does not influence on the foam density. However, a deeper analysis of the results allows detecting that the time has some effect, as the difference in the foam density of experiences 1 and 2 ( $d = -22$ ) is higher than the one in experiences 3 and 4 ( $d = -15$ ). Taking into account this fact, both foaming process variables were considered. The density values of the four foamed samples were linearly correlated with temperature and time values according to the Equation 1.

**Table 1.** Foaming conditions and characteristics of resulting foams

run	Temperature (°C)	Time (h)	Density (kg/m <sup>3</sup> )	E (kPa)
1	170	1.5	79	602
2	210	1.5	57	1553
3	170	2.5	74	1634
4	210	2.5	59	2059
Midpoint				
5	190	2	65	1496
6	190	2	70	1519
7	190	2	63	1389

The model for the foam density ( $\rho$ ) is given by the following Equation 4:

$$\rho = 67.3 - 18.5 \cdot x_1 - 1.5 \cdot x_2 + 3.5 \cdot x_1 x_2 \tag{4}$$

As expected, coefficient ( $x_1$ ) associated with temperature is higher than coefficient ( $x_2$ ) associated with time, and the interaction coefficient of both variables ( $x_1 x_2$ ) is slightly higher than time coefficient.

The difference between the density value predicted by this model for a sample obtained in the conditions of the midpoint of the experimental domain ( $\rho_{\text{predicted}} = 67.3$  kg/m<sup>3</sup>) and the average of the density values of the experiments (5-7) ( $\rho = 66.5$  kg/m<sup>3</sup>), was statistically assessed by a F-test (see Equation 2). The calculated F was 0.05 and the  $F_{(7, 2, 0.05, 2 \text{ tails})}$  tabulated was 19.35. So, it could be concluded that quadratic curvature

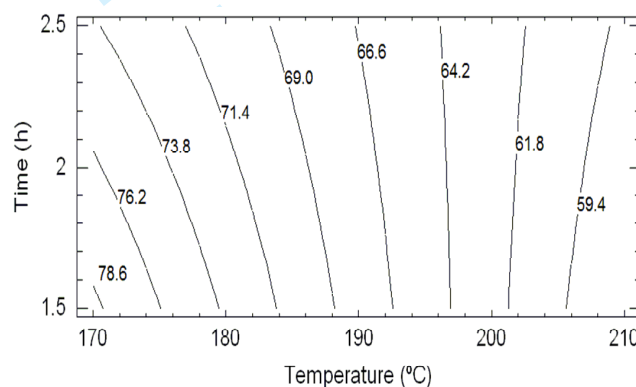


does not exist and therefore a first order model fits to foam density in the considered range.

The model for the density value in function of the temperature ( $T$ ) and the time ( $t$ ) is given by the Equation 5:

$$\rho = 224.63 - 0.81 \cdot T - 34.75 \cdot t + 0.18 \cdot T \cdot t \quad (5)$$

Figure 2 shows the contour map of the foam densities predicted by the model. Foaming temperature had a greater influence on density of the flame retardant foams than foaming time, being specifically over 200 °C. As above mentioned, foams with higher densities should be obtained at lower temperatures. This behavior is in accordance to our previous study on neat polybenzoxazine foams.<sup>9</sup>



**Figure 2.** Contour map for foam density ( $\text{kg/m}^3$ )

It was found that density showed a great dependence on the foaming temperature ( $T_f$ ), decreasing as the temperature increases. In addition, dependence of polymer/gas mixture  $T_g$  and  $T_f$  was observed on the foam porosity, as previously reported for self-foaming poly(phenylquinoxaline)s.<sup>20</sup> Both variables were inter-related between themselves determining that an increase in foaming temperature produces a decreasing in the polybenzoxazine/gas mixture  $T_g$  which leads to higher cells growth and therefore lower density. In reference to foaming time ( $t_f$ ), our results indicated that most of the  $\text{CO}_2$  releases during the first 90 min. From that point on foaming proceeds in a slower way and therefore longer times not significantly affect foam density.

Foam compressive modulus model

The column 5 of Table 1 shows the measured values of the foam compressive modulus obtained in the experiments 1-7. Following the same strategy discussed for the density, the relation between the compressive modulus and the temperature and time is verified to fit also to a first order model.

Both variables exhibit a  $P$ -values  $<0.05$  in the ANOVA analysis (Table 2) indicating that temperature and time have significant influence on the compressive modulus of the foams. It can be observed that for  $\alpha = 0.10$ , the interaction between temperature and time, also has a significant effect on  $E$ , so this factor has been considered.

Table 2. Analysis of variance for compressive modulus (E)

Source	Sum of squares	d.f	Mean square	F-ratio	P-value
$x_1$ :Temperature	473344.0	1	473344.0	98.35	0.0100
$x_2$ : time	591361.0	1	591361.0	122.87	0.0080
$x_1 \cdot x_2$	69169.0	1	69169.0	14.37	0.0631
Lack-of-fit	61.7143	1	61.7143	0.01	0.9202
Pure error	9626.0	2	4813.0		
Total error	1.14356E6	6	3229.24		

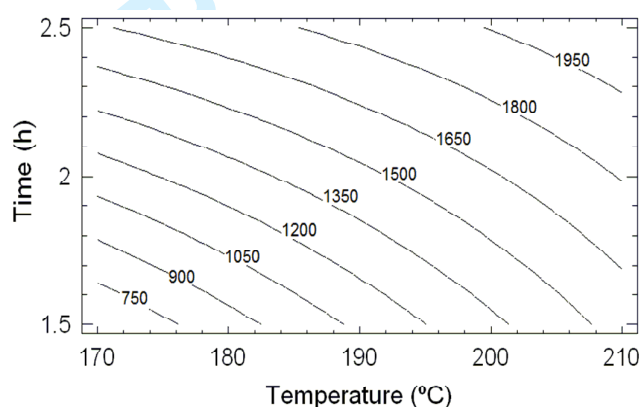
$R^2 = 98,31\%$

The model for the compressive modulus ( $E$ ) is given by the following Equation 6, where the values of the variables are specified in their original units.

$$E = -8338.43 + 43.5 \cdot T + 3267.5 \cdot t - 13.15 \cdot T \cdot t \tag{6}$$

Figure 3 shows the contour map for compressive modulus of the foams. Both  $T_f$  and  $t_f$  exhibit similar influence on the compressive modulus of the polybenzoxazine foams. It is possible to observe that higher values of  $E$  should be obtained when the foaming process takes place at higher temperatures and times. The optimum value predicted by the model for  $E$  is 2061.6 kPa at 210 °C and 2.5 h.

The mechanical properties of foams depend on their structure, the properties of the solid material of which the cells are made and the factors related to the test. The solid material mainly determines the Young's modulus, the yield strength and the fracture strength.<sup>11</sup> To relate and evaluate the relation between morphology and properties of the foams is important to consider some cellular structure parameters such as the size and shape of the cells, apparent density, type of cells (open or closed cells), isotropic or anisotropic structure, cell distribution and cell wall thickness.<sup>21</sup> In turn, foam properties are also affected by the test characteristics *i.e.*, rate of strain, rate of deformation, temperature, sample conditioning, among the most important. Regarding to solid material factors, foam theory states that the compressive properties are directly proportional to their relative density, that is,  $E$  and  $\sigma$  increase with the relative density fitting a mathematical equation in which the fitting constants vary according to the type of foam and the cellular structure.<sup>11</sup>



**Figure 3.** Contour map for foam compressive modulus (kPa)

In our case, the polybenzoxazine foams followed a completely different trend, given that the compressive modulus increases as the foam density decreases. As also determined in the previous reported neat foams,  $T_f$  and  $t_f$  are significant parameters that control the foam morphology and the final foam properties because the foaming and crosslinking processes occur simultaneously. At the beginning, the  $\text{CO}_2$  formation and ring-opening of the oxazine groups start at the same time and proceed in a fast way. Once all the  $\text{CO}_2$  is released, the formed resin continues curing until the selected  $t_f$ . At this point, the network reaches a certain degree of crosslinking that is clearly dependent on  $t_f$ . Hence, an increase in the  $T_f$  and  $t_f$ , results in a higher crosslinking degree of the resin and consequently in higher compressive properties.

Surprisingly, the crosslinking degree of the base polymer had a greater influence on the compressive modulus than the cellular structure of the foam. As observed in Fig. 3, the compressive modulus continually increases with time and temperature. Thus, the main effect that influences the modulus of the foam is the degree of crosslinking, and the variation in  $T_f$  and  $t_f$  are the main causes. To gain more insight about the crosslinking degree of the foams, their glass transition temperature ( $T_g$ ) were determined by DSC and their resulting values are summarized in Table 3. In general, the  $T_g$  of the foams increases as  $T_f$  and  $t_f$  increases too, and the difference of  $T_g$  values becomes more significant at higher temperatures. For instance, at 210 °C the  $T_g$  of the sample foamed (run 2) at 1.5 h is 187 °C while the  $T_g$  of the sample foamed (run 4) at 2.5 h is 213 °C. These results indicate that at lower  $T_f$  and  $t_f$  the obtained foams are not totally crosslinked or the achieved crosslinking degree is lower. For higher  $T_f$  and  $t_f$  the crosslinking gradually rises up to reach almost fully crosslinked materials.

**Table 3.**  $T_g$  and LOI values of polybenzoxazine foams

Run	Temperature (°C)	Time (h)	$T_g$ (°C)	LOI (% O <sub>2</sub> )
1	170	1.5	150	28.1
2	210	1.5	187	31.2
3	170	2.5	159	28.4
4	210	2.5	213	31.4
5	190	2	179	29.1
8	150	2	140	29.4
9	230	2	248	31.9
10	190	1	166	28.5
11	190	3	184	29.8

*Foam compressive strength model*

In this case, to correlate the compressive strength of the foams ( $\sigma$ ) with the foaming temperature and time it was necessary to postulate a model of second order as the indicated in Equation 3. To evaluate the coefficients, four additional experiments were carried out to complete the central composite design ( $2^2 + 3$  center point + 4 star points). The results of the compressive strength of the foams and the experimental design are included in the Table 4.

The model for the foam compressive strength with all significant effects is given by the Equation 7:

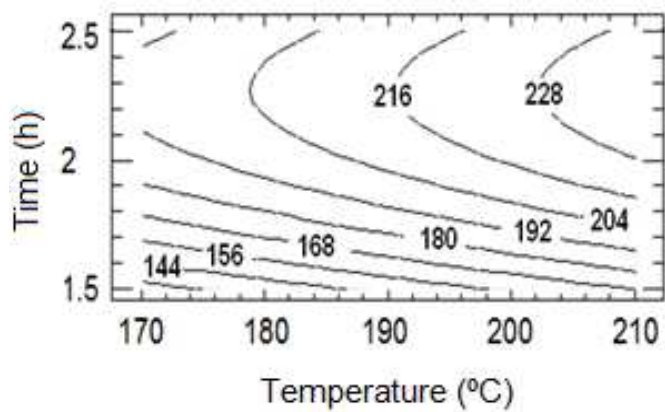
$$\sigma = -553.95 + 1.03 \cdot T + 504.84 \cdot t - 110.89 \cdot t^2 \quad (7)$$

The temperature quadratic term ( $T^2$ ) and the interaction temperature\*time term ( $T \cdot t$ ) were rejected because they presented P-values  $> 0.05$  in the ANOVA analysis. Figure 4 shows the contour map for compressive strength of the foams. It is possible to observe that higher values of the compressive strength ( $\sigma$ ) should be obtained when the foaming process has place at higher temperatures and times. Both  $T_f$  and  $t_f$  had similar influence on the  $\sigma$  until *ca.* 2.1 h. From that, the variations on  $\sigma$  values seem to be somewhat affected by  $t_f$ . The optimum value predicted by the model for the  $\sigma$  is 244.4 kPa at 219 °C and 2.3 h. Implementing this statistical approach with ANOVA revealed the influence of foaming parameters on the foam properties.

**Table 4.** Central composite design, along with the compressive strength values for the foams

Run	Temperature (°C)	Time (h)	$\sigma$ (kPa)
1	170	1.5	95.9
2	210	1.5	186.1
3	170	2.5	187.7
4	210	2.5	210.2
5	190	2	199.5
6	190	2	193.0
7	190	2	203.4
8	150	2	210.6
9	230	2	246.9
10	190	1	115.1
11	190	3	206.5

Again, it was detected a similar trend for the compressive strength to that presented by the compressive modulus of the foams. The highest values of compressive strength correspond with the highest crosslinking degrees, but not with the highest densities. As already discussed, the influence of the crosslinking degree was more meaningful in establishing the compressive strength of the foams than a variation in cellular structure.



**Figure 4.** Contour map for foam compressive strength (kPa)

*Flame retardant properties*

Flammability of polybenzoxazine foams with the same phosphorus content of 1% P, was assessed by the limiting oxygen index (LOI) test. The results have been collected in Table 2. The addition of DOPO-2Me to polybenzoxazine foams had a positive impact on their flammability since the LOI values were found to be ranging from 28.1 to 31.9. These values are higher than those for similar neat polybenzoxazine foams previously reported of 23.6.<sup>10</sup> Such flammability improvement is result of the excellent flame retardant effect of the phosphorus compound that on burning forms a glass like polyphosphoric layer that promotes the formation a protecting char during combustion.<sup>22</sup> As the LOI values did not undergo significant differences, the statistical model is not worth considering.

Usually the LOI is a characteristic of the polymeric material, however it has been reported that for foamed materials the determination of the LOI not only depends on the test characteristics and the environment factors but also on sample density and structure.<sup>23</sup> In this way, LOI value increases with the density. In our case the LOI values of the polybenzoxazine foams were found to be more dependent on a change in the degree of crosslinking than on density, with the exception of the foam sample with the highest density (88.9 kg/m<sup>3</sup>). Thus the highest recorded LOI values correspond to the highest foaming times and temperatures, which in turn are related to the highest degrees of crosslinking of the foams.

**Conclusions**

Polybenzoxazine foams based on the renewable diphenolic acid and an organophosphorus compound were prepared. Thermal polymerization provided not only

crosslinking but also the *in-situ* generation of the blowing agent. A statistical design approach was employed to establish the influence of the foaming parameters on the density, compressive strength and compressive modulus of the foams. The density and the compressive modulus were well fitted to a simple linear model, while the compressive strength required a model of second order. Moreover, it was found that the crosslinking degree of the base polymer exerted a greater influence on the mechanical performance of the foams than the cellular structure.

T<sub>g</sub> of the foams was significantly influenced by the crosslinking degree of the polybenzoxazines, which in turn especially varied with the foaming temperature. The addition of the organophosphorus compound conferred flame retardancy to all the materials.

The obtained results demonstrate the possibility of producing and simulating flame retardant polybenzoxazine foams with good mechanical properties.

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### Conflict of interest

None declared.

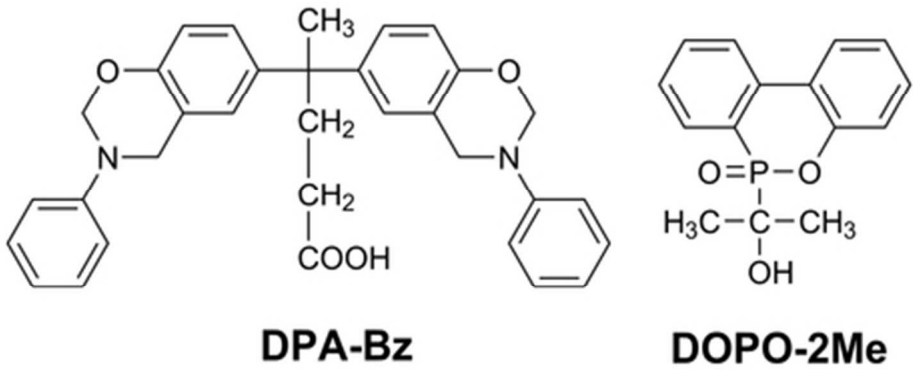
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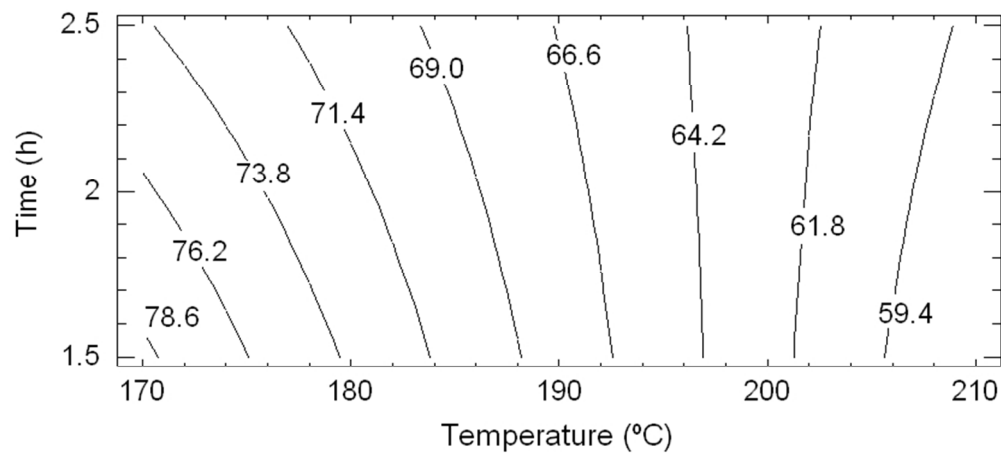
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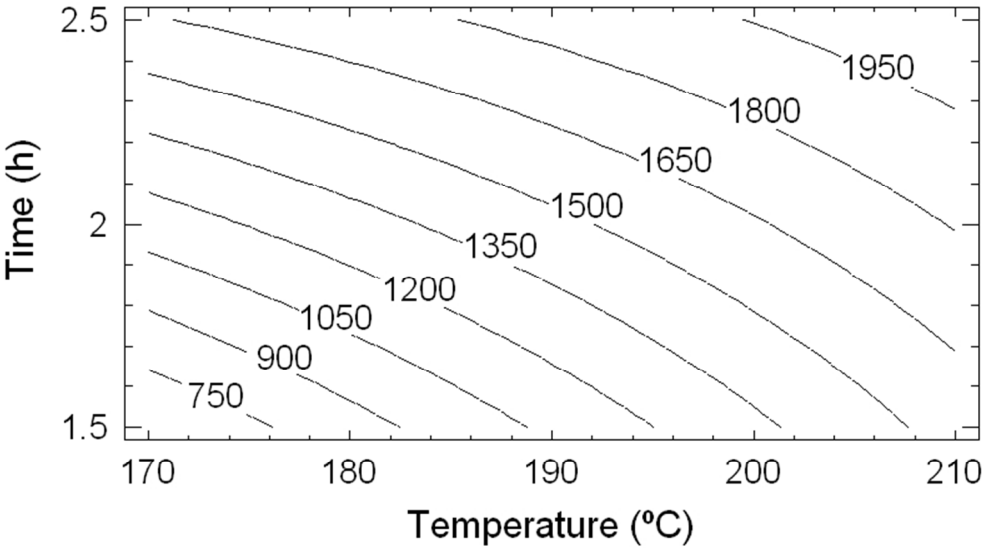
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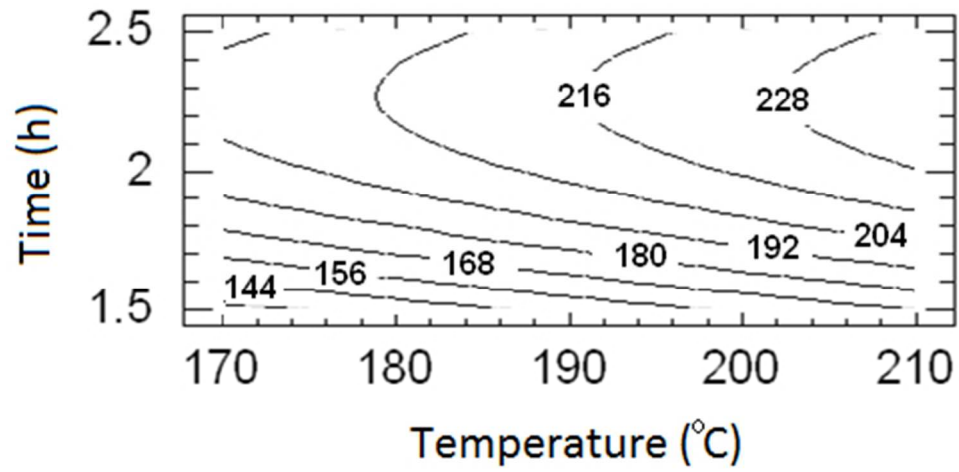
38x16mm (300 x 300 DPI)



141x66mm (150 x 150 DPI)



135x75mm (150 x 150 DPI)



126x62mm (96 x 96 DPI)

Table 1. Foaming conditions and characteristics of resulting foams

run	Temperature (°C)	Time (h)	Density (kg/m <sup>3</sup> )	<i>E</i> (kPa)
1	170	1.5	79	602
2	210	1.5	57	1553
3	170	2.5	74	1634
4	210	2.5	59	2059
Midpoint				
5	190	2	65	1496
6	190	2	70	1519
7	190	2	63	1389

Table 2. Analysis of variance for compressive modulus (E)

Source	Sum of squares	d.f	Mean square	F-ratio	P-value
$x_1$ :Temperature	473344.0	1	473344.0	98.35	0.0100
$x_2$ : time	591361.0	1	591361.0	122.87	0.0080
$x_1.x_2$	69169.0	1	69169.0	14.37	0.0631
Lack-of-fit	61.7143	1	61.7143	0.01	0.9202
Pure error	9626.0	2	4813.0		
Total error	1.14356E6	6	3229.24		

$R^2 = 98,31\%$

**Table 3.** Tg and LOI values of polybenzoxazine foams

Run	Temperature (°C)	Time (h)	Tg (°C)	LOI (% O <sub>2</sub> )
1	170	1.5	150	28.1
2	210	1.5	187	31.2
3	170	2.5	159	28.4
4	210	2.5	213	31.4
5	190	2	179	29.1
8	150	2	140	29.4
9	230	2	248	31.9
10	190	1	166	28.5
11	190	3	184	29.8



**Table 4.** Central composite design, along with the compressive strength values for the foams

Run	Temperature (°C)	Time (h)	$\sigma$ (kPa)
1	170	1.5	95.9
2	210	1.5	186.1
3	170	2.5	187.7
4	210	2.5	210.2
5	190	2	199.5
6	190	2	193.0
7	190	2	203.4
8	150	2	210.6
9	230	2	246.9
10	190	1	115.1
11	190	3	206.5