**1 Introduction**

Nowadays, reduction of fuel consumption is a key parameter in aircrafts design. It involves the use of new materials both lighter and more efficient. Because of their excellent specific properties, composite materials are widely used in the aerospace industry. Composites were traditionally manufactured; either by manual lamination (bottom-end) or autoclave consolidation (higher-end). For the past 30 years in the aerospace industry, autoclave manufacturing has been predominant. Nowadays, new techniques for liquid molding such as RTM ("Resin Transfer Molding") are being introduced to make high quality parts (even better than autoclave composites) at a lower cost. One of the several advantages of this method is the design flexibility that allows for the use of three-dimensional reinforcements instead of the usual multi-ply laminates. Using new 3D reinforcements, high performance composites for structural applications are fabricated.

The main difficulty with manufacturing composites by RTM is the presence of voids in the parts [1]. Voids have a significant effect on the properties of structural composites [2]. Three main causes have been identified for void formation: the inclusion of air during the impregnation of the reinforcement [3-5], the presence of solvents in the resin [6-7] or the volatilization of gases due to the chemical reaction [8]. In the RTM process, applying a consolidation pressure in the mold after injection helps to dissolve Volatile Organic Compounds (VOCs) generated during polymerization but it is often observed that porosities appear on the composite parts even when a consolidation pressure is applied. Henry's law [9] indicates that the amount of gas that can be dissolved in a liquid is proportional to the pressure exerted by the gas on the liquid (at constant temperature and saturation). Therefore, a maximum amount of gas molecules can be dissolved in the liquid resin. It is then required to study this phenomenon in order to bring a better understanding of porosities formation during processing by RTM and more generally liquid composite molding (LCM).

**2 Materials**

In this work, two resin systems were studied. Both are used in the aerospace industry to manufacture composite parts by LCM

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**Keywords:** RTM, porosity, polymerization, VOC, gas, dissolution
high temperature (205 °C). As most thermosets, epoxies are prone to generate VOCs during processing. VOCs can be generated by solvents dissolved in the liquid monomer or gases generated during the chemical reaction. In both cases, gas molecules can form gas bubbles in the liquid resin resulting in porosities in the final part. It is therefore necessary to study and understand bubble formation and to identify significance of the processing parameters on the phenomenon.

In order to study the impact of the curing temperature on the porosity formation, the epoxy resin was first modeled from DSC scans using Kamal-Sourour cure kinetic (see eq. 1):

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m). (\alpha_{max} - \alpha)^n$$ (1)

$$k_i = A_i e^{-E_i/RT} \quad i = 1,2$$ (2)

where m and n are the orders of the reaction and $k_i$ and $k_2$ are the rate constants described by the Arrhenius equation (see eq. 2).

### 2.2 Phenolic resin

The second resin tested in this study is a phenolic resin of resol type. In this case, a polycondensation reaction takes place during the cure which generates H$_2$O as primary by-product and VOCs such as phenol, formaldehyde and methanol. The polycondensation reaction of phenol generates up to 20% of H$_2$O in weight. Curing at a temperature above 100 °C and atmospheric pressure will yield water vapours resulting in large quantity of porosities.

To study this phenolic resin, a cure kinetic model was created from DSC scans. In this case a $n^{th}$ order catalytic model was found to describe appropriately the cure behavior (see eq. 3), where n is the order of the reaction and $k_i$ the rate constant (see eq. 2).

$$\frac{d\alpha}{dt} = k_i. (\alpha_{max} - \alpha)^n$$ (3)

### 3 Experimental technique

To quantify the mass loss during the cure, thermogravimetric analysis (TGA) was carried out on both resins (see FIG. 1 and FIG. 2). It can be seen that the epoxy resin loses around 0.3% of mass when curing at temperatures between 180 °C and 200 °C. This mass loss is related in part to solvent evaporation and also to VOCs release from the chemical reaction. Even though this mass loss seems low, when comparing densities of solid resin and volatiles, the volume of porosities generated by VOCs can be up to 10% of the part when curing in a RTM closed mold. The mass loss of the phenolic resin is however quite different (see FIG. 3). In this case, more than 20% of mass was lost when curing the resin at 120 °C. This substantial loss is related to the polycondensation reaction. It can be observed that contrary to the epoxy resin that stabilizes after 60 minutes (see FIG. 2), the mass loss does not stabilize even after 180 minutes.

In this work, the formation of porosities by VOCs and water vapour was studied using an instrumented RTM tool. This characterization unit named nano RTM mold has a glass window that allows observations of the sample during processing. The tool is designed to cure 20 mL composite samples by applying a cure cycle composed of temperature and pressure steps. This instrument was used to visualize the formation of porosities by VOCs and water content in the resin. The impact of pressure and temperature on the cure cycle and hence on the
formation of porosities was also studied in this work. The epoxy and phenolic resins were cured on the RTM mold. The time of occurrence of the first porosity was observed and recorded for each cure cycles. This study aims to better understand the formation of porosities in liquid resin systems cured at high temperature.

4 Injection results

4.1 Epoxy resin

First, experiments were carried out on the epoxy resin to study the formation of porosities. Table 1 describes the curing parameters used for manufacturing 6 samples. A twenty-minute degassing at 100 °C is applied on the resin prior to each injection. Samples EP-1 and EP-2 were cured at atmospheric pressure and 205 °C. Under these conditions, VOCs generated during the cure can freely evaporate and generate porosities (see FIG. 3(a)). For these two samples, the time at which the first bubble of gas was observed was around 7 minutes after injecting the resin into the heated mold. For samples EP-3 and EP-4, a consolidation pressure of 5 bar was applied immediately right after the resin entered the mold. No porosities were observed on the sample, as shown on FIG. 3(b). In this case, VOCs were instantaneously dissolved into the liquid resin. Applying pressure immediately after the injection seem as a simple solution to avoid the formation of porosities; however it has no practical application. In fact when manufacturing composite parts by resin injection, the liquid polymer has to infiltrate the fibrous reinforcement prior to gelation. Darcy’s flows through porous media are well known for their low impregnation velocities (i.e. Re < 1). Injecting a 1 m² part may take several minutes before the resin reaches the vent port and fully saturates the fibers, while it only takes a few seconds into the nano RTM mold. During the impregnation process, the resin undergoes a certain degree of cure (DoC) and generates VOCs that may not reach the vacuum line. By the end of the injection process, the DoC may be enough to increase the resin viscosity to a certain value. As a consequence, it does not allow the VOCs to be dissolved in the resin. In this case, a very high consolidation pressure is required to eliminate porosities due to the high viscosity of the resin. It is then of interest to define the critical DoC at which the volatiles appear and then can be dissolved by a low consolidation pressure. FIG. 4 shows the curing cycle used for the sample EP-1. After being preheated at 180 °C, the resin is injected into the nano RTM mold at around 3500 seconds. The mold is then heated and maintained at 205 °C to cure the resin. The first porosity was observed at around 3750 seconds (i.e. 250 seconds after the injection). At that instant, the DoC was 8% (see Table 1 and FIG. 4), indicating that an important amount of VOCs are generated at an early stage during the cure. This was also observed on the TGA (see FIG. 1). The last part of the experiment consisted in manufacturing two samples (EP-5 and EP-6), and applying the consolidation pressure 10 minutes after the injection. In this case, even though porosities were observed before applying the 5 bar pressure, 10 minutes were enough to dissolve the VOCs into the still liquid resin. At the end of curing, no porosities were visible on these samples. The process of applying pressure after 10 minutes tested on this work seems to be an appropriate solution. It can dissolve VOCs generated during cure at high temperature of epoxy resins used for LCM. FIG. 4 shows that the first gas appearance is independent of the thermal cycle of the resin and is
only linked to the cure evolution, which indicates that it is due to the chemical reaction. This technique cannot be extrapolated to other resin systems since it depends on the critical DoC, therefore to the chemical reaction.

4.2 Phenolic resin

A second set of experiments were carried out with the phenolic resin to study the influence of degassing and curing conditions on the formation of porosities (see Table 2). Four samples (P1 to P4) were cured using a consolidation pressure of 35 bar. In the case of phenolic resins, the polycondensation reaction leads to water formation that has to be evacuated from the sample or dissolved into the liquid. At a curing temperature of 160°C, a pressure greater than 30 bar is required to keep water in the liquid state and to dissolve it in the sample.

Degassing is frequently used at the beginning of the cure process to reduce the amount of water molecules in the solid material. During the first stage of cure, while the resin is liquid, water molecules are evacuated from the resin by applying a vacuum pressure to the mold cavity. This process eliminates a large quantity of water vapour. However, resin viscosity increases, thus preventing vapour bubbles to move toward the vent port.

The first experiment (sample P1), was carried out without degassing the resin. As shown in FIG. 5(a), this sample presents a high degree of porosities. Sample P4 was made using a 12 hour degassing cycle at 80°C. FIG. 5(d) shows a transparent sample P4 with no visible porosities. This sample served as a baseline to study the porosity content. This set of parameters seems ideal for processing the material. However, at the end of degassing, the resin reaches a DoC 28%, close to gelation. These processing conditions have no practical use for LCM. Hence, degassing conditions were tested at different temperatures (sample P2) and times (sample P3). In these two cases, the DoC at end of degassing was 1% and 6% respectively. The assumption was made that the defects are pockets of liquid water. The observed mass content was 5% and 2% respectively. This indicates that an optimum degassing cycle exists allowing to evacuate most vapors while keeping resin viscosity low.

It is also interesting to study the beginning of porosity formation. Fig. 6 shows two curing cycles of samples P1 and P3. It can be seen that even if different temperature profiles were used, the critical DoC (i.e. DoC at which the first porosity is observed), is still the same for both samples. In fact the first porosity was observed at around 80% of cure for both curing cycles. This demonstrates that porosities are formed at high temperature when the resin reaches a solid state. This can also be seen on the microscopy pictures of Fig. 7. These porosities are in fact cracks in the polymer network leading to discontinuities in the material. Sample P1 without degassing process presents important cracks up to 1 mm long. These cracks reduced in length with the degassing process. Sample P4 with 12 hours degassing does not present any crack.

5 Conclusion

Similar analyses were carried out in the past for pre-preg material [10], with viscosities and VOC contents dissimilar to resins used for LCM. The characteristic of pre-preg material is its B-stage prior to be cured. At that point, most of the solvents diluted in the resin are evaporated prior to using the material.
In this study, two aerospace resins were characterized using novel equipment to allow the identification of a critical degree of cure at which VOCs or defects appear. In the case of the epoxy resin, the experiments showed that this critical DoC of 8%, which is independent of the thermal history. These VOCs are the consequence of the volatiles generated by the chemical reaction during polymerization. An evolved gas analysis could confirm the nature of the VOCs. It was also observed that a critical pressure exists allowing the dissolution of the VOCs into the liquid resin, therefore avoiding the formation of porosities. Moreover, this pressure does not need to be applied before the appearance of the VOCs. It was hypothesized that the pressure has to be applied prior to resin gelation, otherwise the porosities formed will remain on the part. Regarding the phenolic resin, polycondensation made the dissolution of the VOCs more complicated. In this case, pressure, temperature and degassing have to be combined in order to minimize the formation of porosities. As in the epoxy resin, the critical DoC is the same for all the tested conditions of manufacturing. Degassing time and temperature has an important influence on the length and the quantity of porosities found in cured samples. More experiments are required to see the influence of degassing on the formation of cracks and the influence of the consolidation pressure on the dissolution of H₂O. The quantity of removed molecules is limited by the viscosity of the resin which is increasing with the degree of cure and a too high viscosity leads to poor injection.

For both resins, the consolidation pressure required has a direct impact on the design of the mold and on the sealing system. Moreover, the critic time before applying the pressure is also important for the mold filling strategy. This new approach of characterization from a process point of view is a step forward for the optimization of molding cycles in LCM processing.

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References


### TABLE 1 Experiments for studying the cure of epoxy resin on the nano RTM mold and results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Curing temperature (°C)</th>
<th>Consolidation pressure (bar)</th>
<th>Time to application of pressure (min)</th>
<th>Critical DoC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP-1</td>
<td>205</td>
<td>-</td>
<td>-</td>
<td>8.1</td>
</tr>
<tr>
<td>EP-2</td>
<td>205</td>
<td>-</td>
<td>-</td>
<td>5.2</td>
</tr>
<tr>
<td>EP-3</td>
<td>205</td>
<td>5</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>EP-4</td>
<td>205</td>
<td>5</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>EP-5</td>
<td>205</td>
<td>5</td>
<td>10</td>
<td>8.5</td>
</tr>
<tr>
<td>EP-6</td>
<td>205</td>
<td>5</td>
<td>10</td>
<td>11.0</td>
</tr>
</tbody>
</table>

### TABLE 2 Experiments of phenolic samples cures under different conditions in the nano RTM mold and results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Curing cycle (°C)</th>
<th>Temperature during degassing (°C)</th>
<th>Duration of degassing (h)</th>
<th>DoC at end of degassing (%)</th>
<th>Time to application of pressure (h)</th>
<th>Residual H₂O weight (%)</th>
<th>Critical DoC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>19.5 h @ 80&lt;br&gt;2h @ 160</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>10</td>
<td>80.7</td>
</tr>
<tr>
<td>P2</td>
<td>2.5h @ 50&lt;br&gt;15h @ 80&lt;br&gt;2h @ 160</td>
<td>50</td>
<td>2.5</td>
<td>&lt; 1</td>
<td>15</td>
<td>5</td>
<td>86.0</td>
</tr>
<tr>
<td>P3</td>
<td>13.5h @ 80&lt;br&gt;2h @ 100&lt;br&gt;2h @ 120&lt;br&gt;2h @ 140&lt;br&gt;2h @ 160</td>
<td>80</td>
<td>2</td>
<td>5.6</td>
<td>11.5</td>
<td>2</td>
<td>79.5</td>
</tr>
<tr>
<td>P4</td>
<td>12h @ 80&lt;br&gt;2h @ 160</td>
<td>80</td>
<td>12</td>
<td>28.2</td>
<td>12</td>
<td>0</td>
<td>-</td>
</tr>
</tbody>
</table>
FIG. 1 Thermogravimetric analysis of epoxy resin during cure.

FIG. 2 Thermogravimetric analysis of phenolic resin during cure.
FIG. 3 Epoxy samples cured without pressure, EP-1 (a) and with consolidation pressure, EP-3 (b).

FIG. 4 Cure analysis of epoxy resin with different thermal cycles and observation of the first gas bubble (void).
FIG. 5 Phenolic samples cured with 35 bar of pressure without degassing (a) and with degassing (b), (c), (d).

FIG. 6 Cure analysis of phenolic resin with two different temperature cycles.
FIG. 7 Microscopy analysis of cured samples under different degassing conditions (see Table 2).