

POROSITY CONTROL BY PROCESS PARAMETERS

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ABSTRACT

The main difficulty in the manufacturing of RTM composite parts lies in the appearance of voids in the parts. Some of these voids are caused by chemical and physical phenomena taking place during polymerization. In this study, a resol phenolic resin was investigated by thermogravimetric analysis (TGA). The results allowed making assumptions on the nature of the volatile content of the resin and on the release mechanism of volatiles at atmospheric pressure between 40 °C and 240 °C. RTM injections were carried out with a mold equipped with a glass window. The process parameters were chosen based on TGA results. The different phenomena that occur during cure, especially the appearance of voids or defects, were observed directly through the glass window. The results obtained showed that the degassing is the key parameter related to the porosity ratio, that defects always appear around 80 % of cure, and that degassing until gelation gives parts with no porosities.

1 INTRODUCTION

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 aerospace industry, manufacturing using autoclave process has been predominant. Nowadays, new techniques using liquid molding, such as RTM ("Resin Transfer Molding"), were introduced to achieve high-end quality parts but at much lower costs than the autoclave. One of the several advantages of this method is the flexibility of the design, which allows the use of three-dimensional reinforcements, instead of the usual multi-ply laminates. With new 3D reinforcements, high performance composites for structural applications are manufactured.

The main difficulty with manufacturing composites using RTM lies in the appearance of voids in the parts [1]. Voids have a significant impact on the properties of structural composite parts [2]. Three main causes have been identified for void formation: entrapment of air during the impregnation of fibers [3-5], presence of solvents in the resin [6, 7] or volatilization of gases due to the chemical reaction [8]. In the RTM process, applying a consolidation pressure in the mold after injection helps dissolving the volatile organic compounds (VOCs) generated during polymerization; however, it is often observed that

porosities appear on the composite parts even if consolidation pressure is applied. Henry's law [9] indicates that the amount of gas that can be dissolved in a liquid is directly proportional to the pressure exerted by the gas on the liquid (at constant temperature and saturation). Thus, there is a maximum amount of gas molecules that can be dissolved in the liquid resin. It is therefore necessary to study this phenomenon in order to understand the formation of porosities during the RTM process, and more generally, liquid composite molding (LCM).

In this paper, thermogravimetric analyses (TGA) are carried out in order to quantify the volatiles that can be released by the resin and to determine the mass loss as a function of the degree of cure. As a result, the RTM process parameters (temperature, pressure, time settings) can be set to limit the impact of volatiles on the residual porosity in parts. Injection of resin is made in a RTM mold equipped with a glass window. Microscopy analyses and density measurements are made to confirm the impact of process parameters on the residual porosity.

2 MATERIAL

In this study, the material tested is a resol type phenolic resin. The reaction during cure is a polycondensation that generates H_2O as primary by-product and VOCs such as phenol, formaldehyde and methanol. The polycondensation reaction of phenol generates up to 20 % of volatiles by weight. Curing the resin at a temperature above 100 °C and atmospheric pressure leads to the generation of large quantities of water vapor, yielding significant porosities. This is due to the gelation of the resin that traps the water vapor bubbles in the resin (Fig. 1).

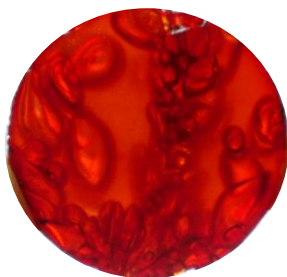


Figure 1: Polymerized phenolic resin with entrapped bubbles.

A simple experiment is conducted to evaluate the initial volatile content. All weight measurements were carried out using a Satorius scale with an accuracy of 0.1 mg. A quantity of about 12 mg is placed under vacuum with a maximum temperature of 48°C (Fig.2). At these temperature and pressure (0.09 bar) conditions, the volatiles are removed from the resin without any polymerization. When boiling is no longer observed, the resin is weighed again. The total mass loss is 4.97 %. Volatiles include methanol and formaldehyde, but mainly water. All these measurements are summarized in Table 1.

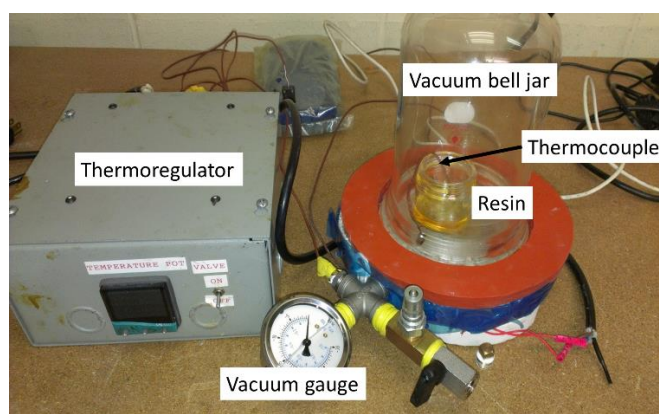


Figure 2: Pressure-temperature setup for initial volatile content evaluation in phenolic resin.

Description	mass (g)
Container without resin	81.4073
Container with resin	93.8119
Resin	12.4046
Container with resin after degassing	93.1661
Resin on the thermocouple	0.0292
Weight loss by degassing	0.6166
Relative weight loss (%)	4.97

Table 1: Measured masses for initial volatile content evaluation.

DSC analyses are carried out on the non-degassed and the degassed resin in order to verify that no polymerization happens during degassing. It is critical that there is no polymerization in order to guarantee the initial volatile content measurement, since the by-products generated during polycondensation would increase the mass loss. Fig.3 shows the results of two samples of non-degassed resin and one sample of degassed resin; the three curves are similar. Moreover the reaction enthalpies and the maximum temperatures reported in Table 2 are very similar for both non-degassed and degassed resins. From these results, we can clearly state that no polymerization has occurred during the measurement of the initial volatile content.

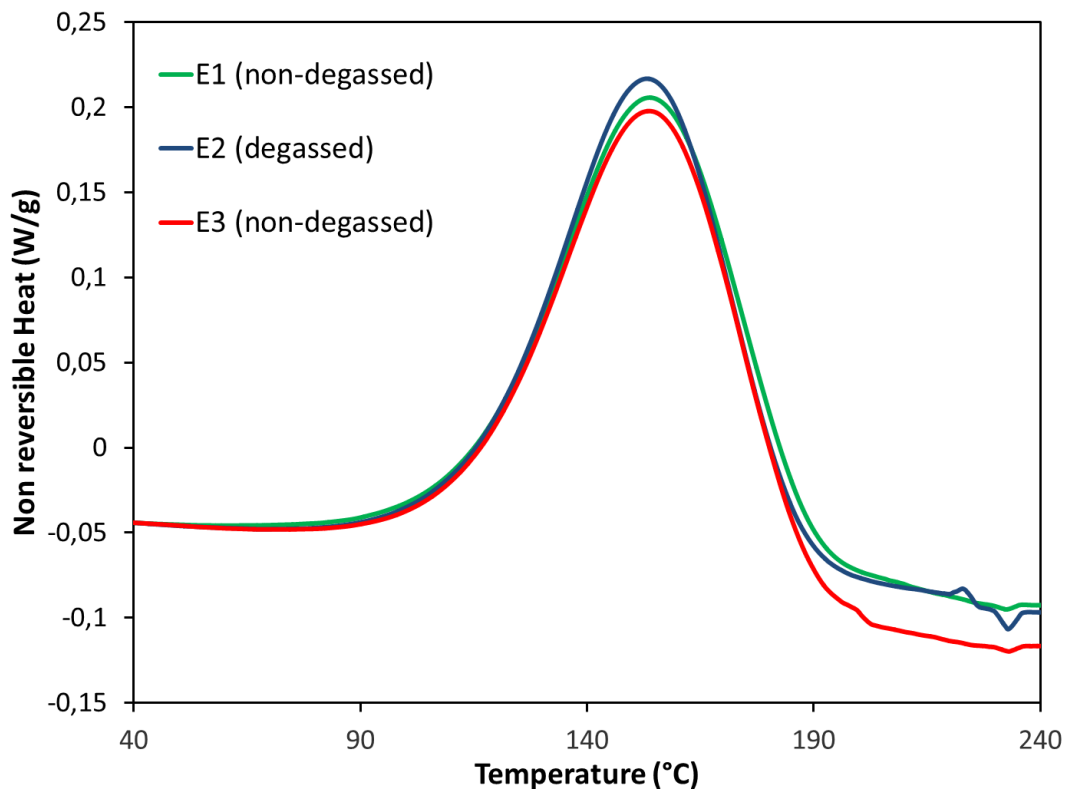


Figure 3: Evolution of non-reversible heat flow for degassed (blue) and non-degassed (green and red) phenolic resin.

Sample	Degassing	Heating rate (°C/min)	ΔH (J/g)	T max (°C)
E1	No	3	257.3	154
E2	Yes	3	256.2	154
E3	No	3	259.0	155

Table 2: Reaction enthalpy and peak temperature for non-degassed and degassed phenolic resin following the initial volatile content extraction.

4 EXPERIMENTAL SETUP

Porosities in parts processed by RTM (excluding the impregnation of the fibers) result from the presence or formation of volatiles during the resin cure. To better understand this phenomenon, TGA analyses were performed. A minimum of 20 % of weight loss is expected during polymerization for this resin. During these experiments, the weight loss is monitored, and thus the release of volatiles is given as a function of the temperature. Therefore, the release of volatiles can be related to the quantity of gas that will be trapped in the RTM mold during the resin cure, with the exact same pressure and temperature conditions than in TGA experiments. These results are used to adjust the process parameters so as to limit the impact of the volatiles during RTM resin cure. Two heating ramps (1 °C/min and 3 °C/min) were used to distinguish the effect of the temperature from the degree of cure. The tests were carried out on Q500 TGA from TA Instruments under nitrogen atmosphere (60 cc/min for the furnace and 80 cc/min for the balance). For each test, 5 to 6.5 mg of resin was placed in an aluminium crucible in the TGA chamber.

The formation of porosities due to VOCs and water vapour was studied using an instrumented RTM tool designed for this purpose. This characterization unit named “Nano RTM mold” has a glass window that allows observing the sample during the process. The tool is designed to cure 20 mL of composite or resin samples by applying temperature and pressure steps. In this work, the impact of pressure and temperature on the cure cycle and hence the formation of porosities was studied. The onset time of the first porosity was observed and recorded for each cure cycle. This study aims to better understand the formation of porosities in liquid resin systems cured at high temperature. The main focus is the influence of the process parameters (time settings, temperature and pressure). A thermocouple placed in a wall of the cavity allows measuring the temperature in the mold. A series of eight experiments were performed as described in Table 3. For each sample, the table indicates the temperature cycle (including the degassing stage), the temperature during degassing and its duration (whether it occurs in the injection pot or in the mold), the degree of cure (DoC) at the end of the degassing, the time when pressure is applied in the cure cycle, the critical DoC (i.e. when the first defect is visualised through the glass window of the mold) and the relative density of the cured resin. Density is measured for each sample according to ASTM D972 standard. Sample P6 has the highest density so the relative density was defined as $\text{density}_{P_i} / \text{density}_{P6}$. The degree of cure (α) of the resin can be calculated in the TGA and in the Nano RTM mold with a n th-order catalytic model (see eq. 1). This kinetic model was defined from a comprehensive DSC study.

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

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

where t is time, m and n the orders of the reaction, α_{max} the maximum degree of cure achieved by the resin, k_1 and k_2 the rate constants described by the Arrhenius equation (see eq. 2), E_1 and E_2 the activation energies, R the universal gas constant and T the temperature. In addition, the viscosity μ of the resin is modelled using equation 3:

$$\mu = K_1 \cdot \left(\frac{1}{T}\right) \cdot K_2 \cdot e^{K_3 \cdot \alpha^{K_4}} \quad (3)$$

where α is the degree of cure, T is the temperature and K_1 , K_2 , K_3 and K_4 are constants of the model.

Sample	Curing cycle (°C)	Temperature during degassing (°C)	Duration of degassing (h)	DoC at end of degassing (%)	Time to apply 25 bar pressure (h)	Critical DoC (%, ± 5%)	Relative density
P1	19.5 h @ 80 2h @ 160	No degassing	0	0	0	80	0.982
P2	2.5h @ 50 15h @ 80 2h @ 160	50	2.5 (injection pot)	< 1	15	86	0.986
P3	13.5h @ 80 2h @ 100 2h @ 120 2h @ 140 2h @ 160	80	2 (injection pot)	5.6	11.5	79	0.993
P4	12h @ 80 2h @ 160	80	12 (mold)	28.2	12	No defects	1.000
P5	13h @ 80 8h @ 100 2h @ 160	80	2 (injection pot)	5.6	No pressure	74	0.993
P6	4.8 @ 90 2 @ 160	90	4.8 (mold)	30	4.8	No defects	1

Table 3 : Experiments of phenolic samples cured under different conditions in the Nano RTM mold – test parameters and results.

5 RESULTS

5.1 Thermogravimetric analysis

Fig. 4 illustrates the mass loss evolution with temperature for two heating rates of 1 and 3 °C/min. Both heating rates lead to a very similar total weight loss of about 22 % \pm 0.7 % (see Table 4). It is therefore possible to conclude that this difference in heating rates has no influence on the total amount of volatiles released. The resulting curves also show that volatiles are released all along the polymerization of the resin, incurring by a regular mass loss. This result is in agreement with the polycondensation mechanism. However, the two curves are not identical, phenolic resin having a complex reaction scheme that involves several components (more than 20) during polymerization. The heating ramp may influence the reaction scheme and thus there may be an impact on the by-product release kinetic.

Fig. 5 shows the weight loss and the modelled viscosity (see eq. 3) for the same experiments as in Fig. 4 (TGA-1 and TGA-4) with respect to the DoC. Three distinct zones can be observed, leading to the following assumptions:

- Zone 1: non-linear weight loss where volatiles and water are released by evaporation. This phenomenon is promoted by the large exchange surface between the resin and the nitrogen carrier gas. Evaporation occurs only in the early stage of curing (less than 3.4 %, see Fig. 5).
- Zone 2: linear weight loss due to the boiling of water in the resin. This zone begins when the temperature reaches 100 °C. Gelation is characterized by a significant increase in viscosity. From a process point of view, gelation is characterized by a 10 % increase in the derivative of viscosity. The evolution of the viscosity in this zone indicates that gelation occurs between 25 % and 35 % of cure. The gelation point marks the end of zone 2.
- Zone 3: non-linear weight loss due to the convection drying of the resin. The gelation zone clearly indicates a change in the phenomenon that controls the evacuation of the water contained in the resin. Indeed, the end of zone 2 corresponds to the gelation point, so the resin is no longer in a liquid state. Hence, the water bubbles cannot grow or travel through the resin and are trapped inside. So, water is extracted from the cavities only by drying of the resin.

Sample	Heating rate (°C/min)	Initial mass (mg)	Total weight loss (%)
TGA-1	1	5.070	22.66
TGA-2	1	5.833	22.21
TGA-3	1	5.432	21.48
TGA-4	3	5.951	21.54
TGA-5	3	6.195	21.33
TGA-6	3	5.814	21.68

Table 4 : Total weight losses for the 1°C/min and the 3°C/min heating ramps.

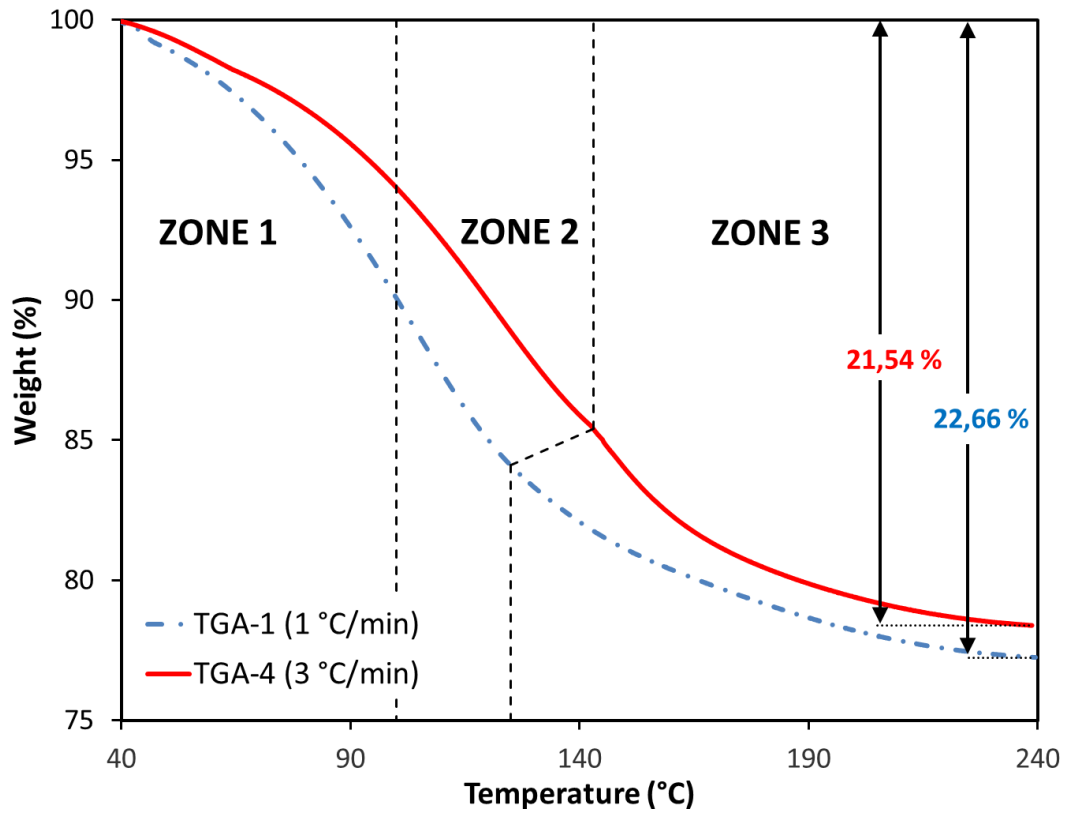


Figure 4 : Weight loss by thermogravimetric analysis under nitrogen for 1 °C/min (TGA-1) and 3°C/min (TGA-4) heating ramps.

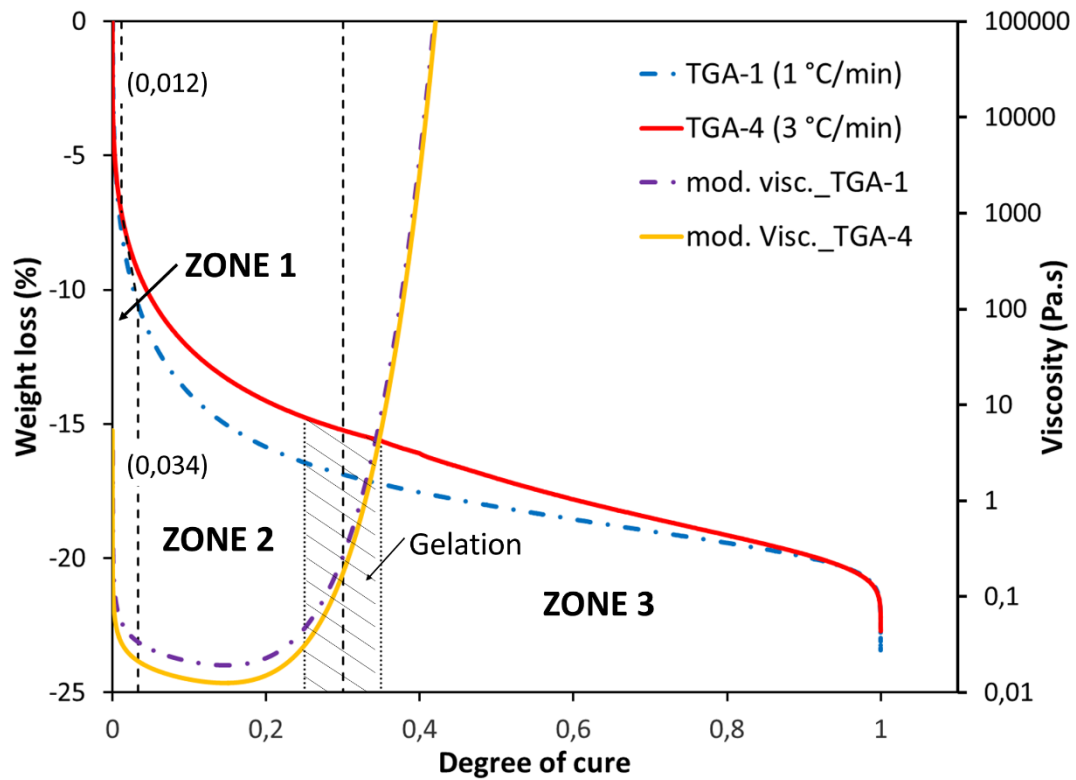


Figure 5 : Weight loss and viscosity model vs degree of cure for 1 °C/min (TGA-1) and 3°C/min (TGA-4) heating ramps.

5.2 Nano RTM mold

Fig. 6 illustrates the evolution of the degree of cure with respect to time for the 6 experiments described in Table 3. On the curing curves, events such as the onset of the first bubble, porosity or defect are identified with diamonds. The times associated at these events are indicated as the critical degrees of cure in Fig. 6. A first sample (P1) is injected without any degassing, and a pressure of 25 bar was applied immediately after injection to ensure that the water is maintained in the liquid state with the temperature increase, keeping a maximum of water and volatile contents dissolved in the resin. No bubbles or porosities were formed prior to the solidification of the resin; however defects appeared around 80 % of cure (Table 3 and Fig.6). As illustrated in Fig. 7, sample P1 contains much porosity.

A second sample (P2) was made with the resin degassed inside the injection pot at a temperature of 50 °C. The main idea of degassing prior to injection is to extract the initial volatile content of the resin that has been measured previously and observed in the very early stage of the thermogravimetric analysis. During this step, a non-negligible amount of volatiles (5 %) can be extracted from the resin without affecting the degree of cure (see Table 1). Therefore, the resin viscosity is not increased, ensuring good injection in the mold (and impregnation of fibers when applicable). The expected outcome of this experiment is a delay in the appearance of defects, due to the deferred saturation of the polymer since 5 % of the volatiles have already been removed. However, the result for sample P2 is quite similar as P1 in terms of critical degree of cure (80 %), taking into account the measurement uncertainty (see Table 3 and Fig.6); the main difference is that visually, the final sample seems to be less porous (see Fig.7).

For sample P3, the resin was degassed until 5 % of cure to extract the initial volatile content of the resin and part of the by-product. The sample looks less porous than P1 and P2 (see Fig. 7), but defects still appear around 80 % of cure (see Table 3 and Fig. 6).

As discussed above in section 5.1, the resin produces by-product all along the polymerization. Consequently for sample P4, the resin was degassed directly into the mold just after injection and until gelation (~ 30 % of cure). This allows removing more than half of the blowing content of the resin. Sample P4 final aspect is transparent with no visible porosities.

The same degassing parameters as for sample P3 were used for P5 with the exception that no pressure was applied after degassing; the objective of this experiment was to observe the influence of pressure. The final result is similar to P3, although the two different tests were carried out at different cure temperature cycles; it seems that the cycle does not affect the critical degree of cure.

A different temperature cycle was set for sample P6 but the same degassing parameters as for sample P4 were used. The final result is a transparent part with no porosities, similar as P4. This shows the significance of the degassing parameters over the thermal cycle.

The relative densities reported in Table 3 confirm the visual inspection results illustrated in Fig. 7; the more the resin is degassed, the lower is the porosity ratio. The density is the same for samples P3 and P5 which confirms that pressure has a little influence after gelation of the resin and that degassing is the key parameter to obtain a final part without porosity.

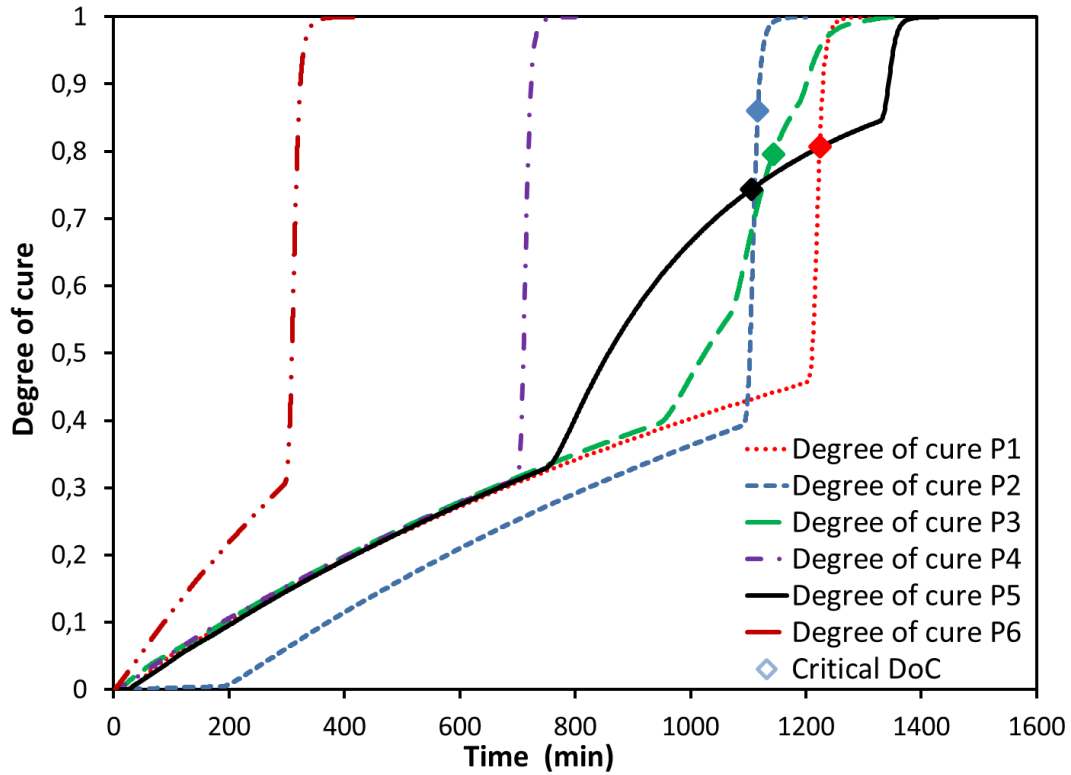


Figure 6 : Evolution of the degree of cure in the Nano RTM mold and critical degree of cure at the onset defect for different experiments (see Table 3).

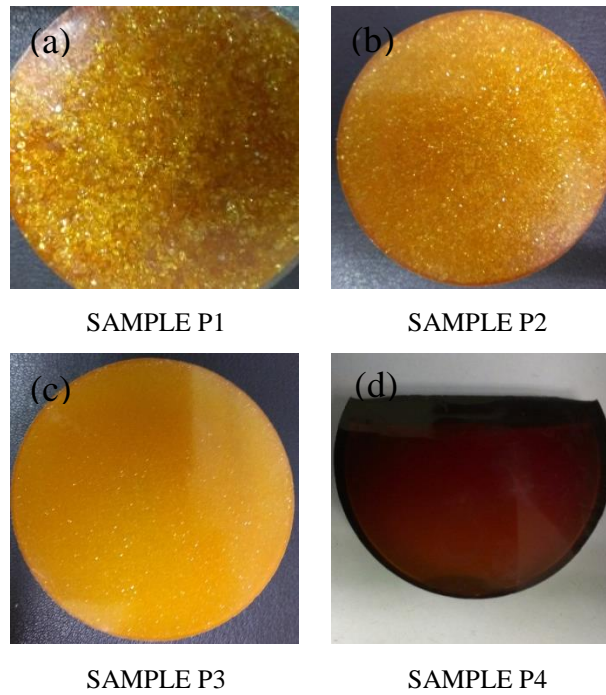


Figure 7 : Phenolic samples cured with pressure at 25 bar without degassing (a) and with degassing (b), (c), (d).

Microscopy observations in Fig. 8 show that the porosities are in fact cracks in the polymer network leading to discontinuities in the material. Sample P1, cured without prior degassing, presents important cracks up to 1 mm long. The crack length is reduced for samples made using a degassing process. Sample P4 with 12 hours degassing presents no cracks. For the resin samples showing defects, the cracks appear around 80 % of cure, whatever the degassing settings (Fig. 6). This suggests that the quantity of volatiles that can be dissolved into the resin may change with the degree of cure, mainly close to 80 % of cure. When the quantity of volatiles dissolved in the resin becomes greater than what can be sustained by the free volume of the polymer, the dissolved content creates internal stresses in the part that lead to breakage in the polymeric network as illustrated in Fig. 9. The free volume is likely composed of voids of different sizes according to a distribution. Some of these voids are probably too small to receive water molecules, but others are large enough for that. When the resin shrinks during cure, the size of voids decreases and the pressure exerted by the water trapped in voids breaks the polymer network at certain locations so that the local stresses can be released in the polymer. Water moves into cracks created by breakage. This displacement is possible through the spaces left unoccupied by the water molecules. This highlights the importance of the degassing process; by degassing until 30 % of polymerization, it is ensured that the quantity of volatiles dissolved inside the resin is smaller than the free volume until the resin is fully polymerized (Fig.10).

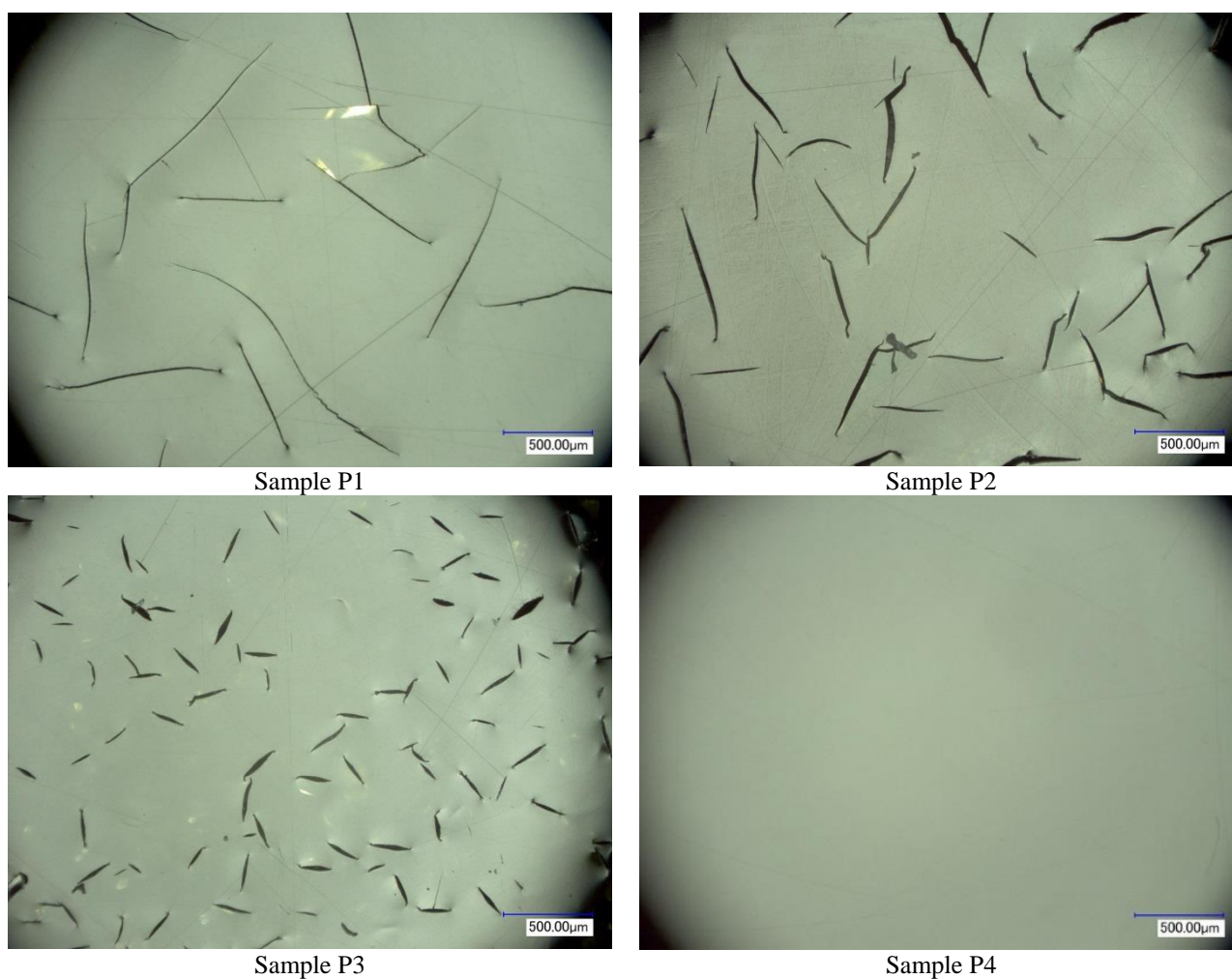


Figure 8 : Optical microscopy analysis of cured samples under different degassing conditions (see Table 3).

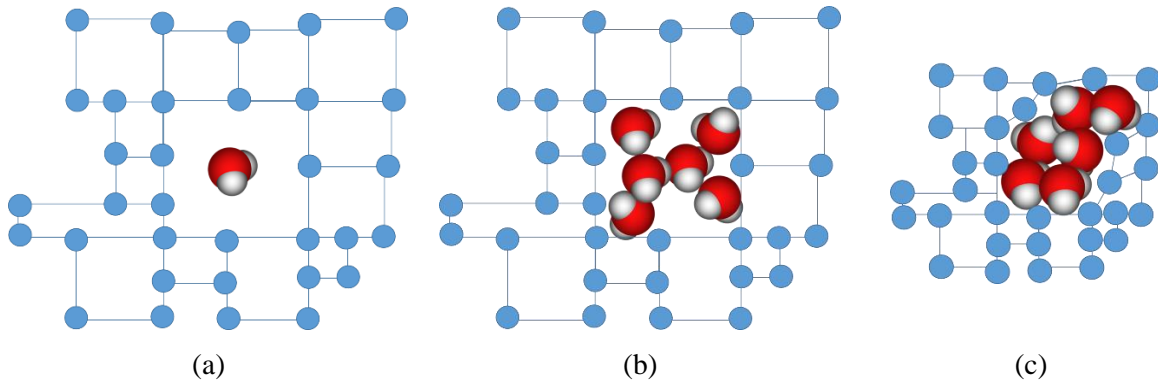


Figure 9: Breakage and deformation of the network (a) due to water quantity increase (b) and free volume decrease (c).

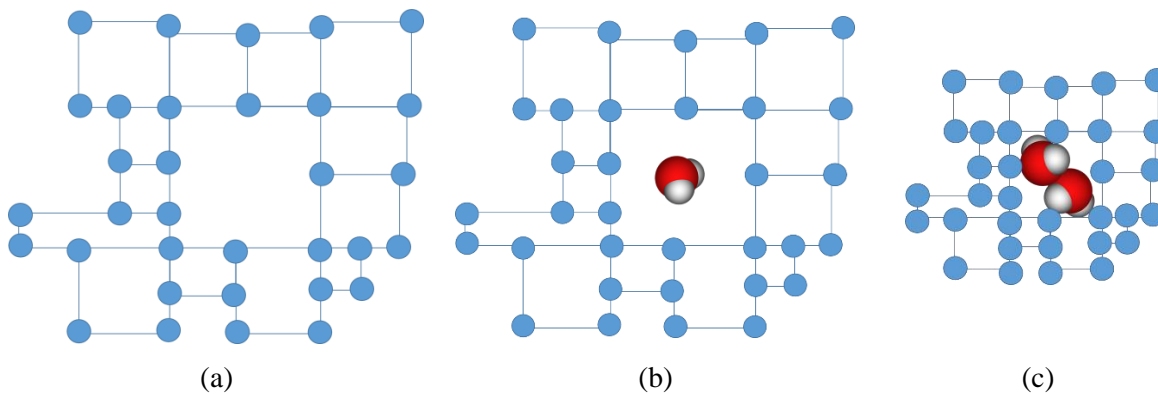


Figure 10: Effect of the degassing on the water content. The presence of the water in the free volume is delayed (a), (b), and the water content never exceeds the free site (c).

6 CONCLUSION

The volatile content that can be released at atmospheric pressure during curing was measured for a resol phenolic resin. TGA results have shown a total weight loss around 22 %, which is the result of volatiles such as water, methanol, formaldehyde or phenol contained initially in the resin, and water produced by polycondensation reaction of the resin throughout curing. Weight loss evolution was also observed with respect to the degree of cure. Analysis of these results led to the selection of some process parameters in order to minimize the residual porosity in parts manufactured by liquid molding. These have been tested by RTM injection. This was performed using an instrumented RTM mold with a glass window. Several experiments were carried out using different process and degassing parameters. It follows that the onset of defects in samples occurs at 80 % cure, when the resin is already solidified. Results show that degassing is the key parameter to obtain samples with minimal porosity; this was confirmed with density measurements of the cured samples. Degassing for up to 30 % of cure produces parts that are free of porosities. However, degassing parameters have an important influence on the size and the quantity of the porosities of the cured samples. Further experiments are needed in order to understand the influence of degassing on the formation of cracks and the influence of a consolidation pressure on the dissolution of H₂O after degassing. The applied pressure has a direct impact on the design of the mold and the closure and sealing system. This new approach in characterization with a process point of view is a step forward for the optimization of molding cycles in LCM processes.

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