VOID GROWTH/COLLAPSE DURING CURING OF AN RTM EPOXY RESIN

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ABSTRACT

Porosities generated during curing are a frequent issue in the processing of composite materials. These porosities (voids) can be due to the volatilization of chemical species during curing and result in lowering the mechanical performance of the material. In this work, porosity formation was studied for a RTM epoxy resin. First, resin curing in a laboratory scale RTM mold was carried out to observe porosity formation and to characterize the effect of pressure and temperature on the void dissolution. Porosity formation was recorded along curing through a glass window on the RTM mold. Then, a mathematical model was used to predict void formation and numerically computed and compared to the experimental results with good agreement between both.

1 INTRODUCTION

Porosity formation is still a critical issue when processing composite materials using RTM [1, 2]. These porosities (voids) have a detrimental effect on the mechanical properties and fatigue of structural composites [3-6]. The two main causes of void formation are the mechanical entrapment of air during impregnation of the reinforcement [7-9] and the volatilization of chemical species during curing [10-12]. This work focuses on the volatilization of the chemical species during curing. Ledru et al. [13] proposed a model to predict the radius evolution of water/air bubbles during curing of prepregs. These bubbles were mainly due to air trapped between layers during layup process and the moisture absorbed by the prepregs before being processed. This work aims to adapt the model proposed by Ledru et al. to the bubbles behaviour during curing using RTM process. First, curing tests were carried out at atmospheric pressure in a RTM mold to observe bubble growth evolution and with a cyclic pressure to find the non-reversible state of the material. Then, the results of the proposed modified model are compared to experimental results.

2 EXPERIMENTAL

2.1 Material

The resin used in this work is a one-part resin that contains a bisphenol F based epoxy monomer and an amine curing agent. The curing agent in the form of solid particles starts to melt at around 110 °C and has a maximum rate of melting at 145 °C. The characterization of Volatile Organic Compounds (VOCs) in the resin carried out with a GC-MS apparatus has shown that acetone and tetrahydrofuran (THF) appear when the resin is heated up, followed by styrene, o-chloroaniline (oCA) and glycidyl phenyl ether (GFE) that appear during curing. oCA is supposed to be a consequence of the melting of the solid particles (i.e. the curing agent) and is considered in this work as the main and unique volatile organic compound released by the resin curing. The distinctive feature of this VOC is that its soluble fraction reacts with the epoxy resin and the melted curing agent reacts with the monomer concurrently.

2.2 Laboratory scale RTM mold injections

A molding apparatus has been designed to experimentally study the volatile-induced porosity formation and behavior during curing. This set-up allows to accurately control cure temperature and consolidation pressure and to visualize gas bubbles formation. The laboratory scale RTM mold (see Figure 1) consists of a closed cavity mold with height and volume of about 15 mm and 20 mL respectively. The liquid resin is injected with pressure. Vacuum can be applied at the outlet port. The resin is preheated in the injection pot prior to injection into the empty mold cavity through a heated hose. A resin catch pot is used to receive the residual liquid resin once the mold cavity is filled; vacuum pressure is initially applied on the mold cavity through this catch pot. After injection, consolidation pressure can be applied to the resin during curing. A resistance temperature detector (RTD) transmitter is placed on the bottom cap of the mold to control the tool heating. The upper mold cover has a transparent window made of 20 mm thick tempered glass to visualize the bubble formation during processing. The center mold cavity has resin inlet and outlet ports connected respectively to the injection pot and resin catch pot. Once assembled, the mold is placed into a ceramic heating belt. A high-resolution camera of 1920 x 1080 Mpx and a combination of 3 macro lenses is placed above the glass window to record the experiments.

The laboratory scale RTM mold was used in this work to characterize porosity formation on the epoxy resin during processing at different temperature ramps and to study the growth/collapse phenomenon regarding the conversion level. Also, the critical conversion level at which pressure has no more effect on the dissolution of the gas into the resin was identified in the laboratory scale RTM mold. The degassing time was 2 hours at 100 °C to maximize the moisture and solvent extraction prior to resin injection. Then, resin was injected into the laboratory scale RTM mold, preheated at 110 °C. After the injection, the mold was heated with a controlled ramp up to the curing temperature of 180 °C. Table 1 lists the curing conditions of samples S1 to S7 with differences as follows: samples S1 to S4 were heated at 2 °C/min while samples S5 to S7 were heated at 1 °C/min. Samples S1, S2, S5 and S6 were cured at atmospheric pressure while the rest of the samples were cured with a cyclic consolidation pressure of 0 to 345 kPa in order to identify at which conversion level the consolidation pressure has no more effect on the bubbles behavior.

After recording all experiments, videos were post-processed with a dedicated Matlab® code. Bubble radius was identified by detecting the number of pixels between the edge of the mold cavity and the edge of the bubble along the cavity radius, in order to calculate the average radius. This post-processing analysis allowed identifying gas bubbles growth with respect to time.

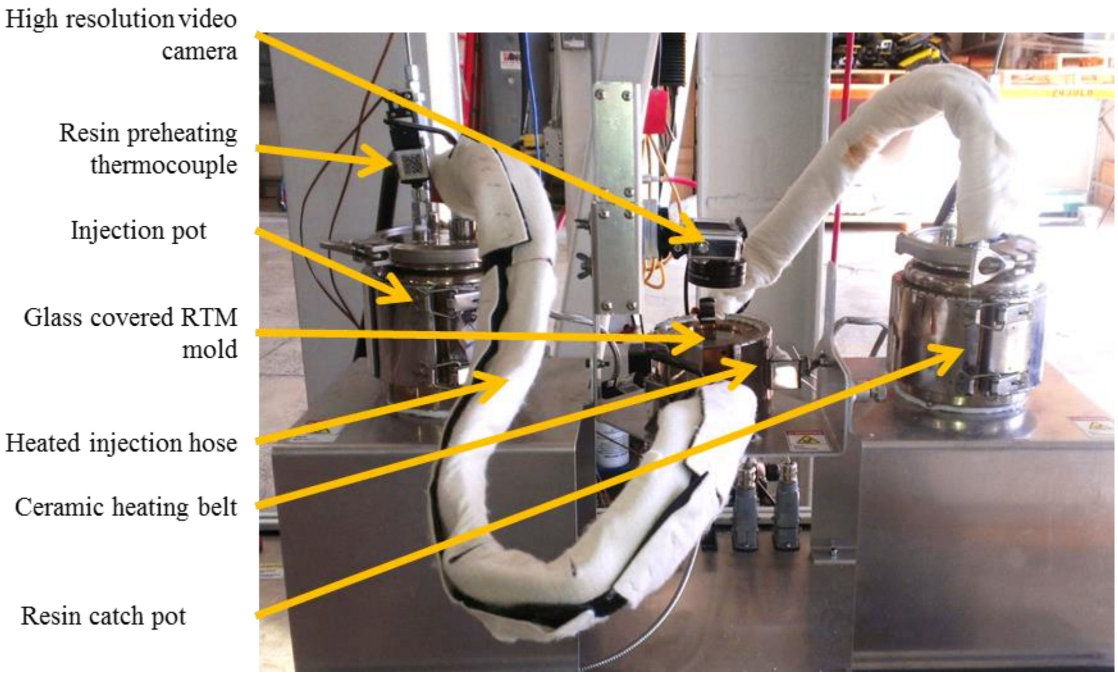

Figure 1. Laboratory scale RTM mold set-up used in this study.

Sample	Curing Ramp (°C/min)	Cyclic Consolidation Pressure (kPa)
S1	2	0
S2	2	0
S3	2	345
S4	2	345
S5	1	0
S6	1	0
S7	1	345

Table 1. Experiments to study the porosity formation on the laboratory scale RTM mold.

3 RESULTS

Figure 2 (a) presents a picture of S1 sample taken 4 minutes after resin injection into the mold exhibiting no porosities in the cavity at this time. In Figure 2 (b), a first gas bubble appears at around 10 minutes after injection. In Figure 2 (c), the number of porosities increases as well as their size at 26 minutes: due to the high reaction rate of the resin, desorption of gas molecules and so nucleation and growth are accelerated at this point. Finally, Figure 2 (d) shows the moment when the resin sample debonds from the glass window at 56 minutes due to chemical shrinkage.

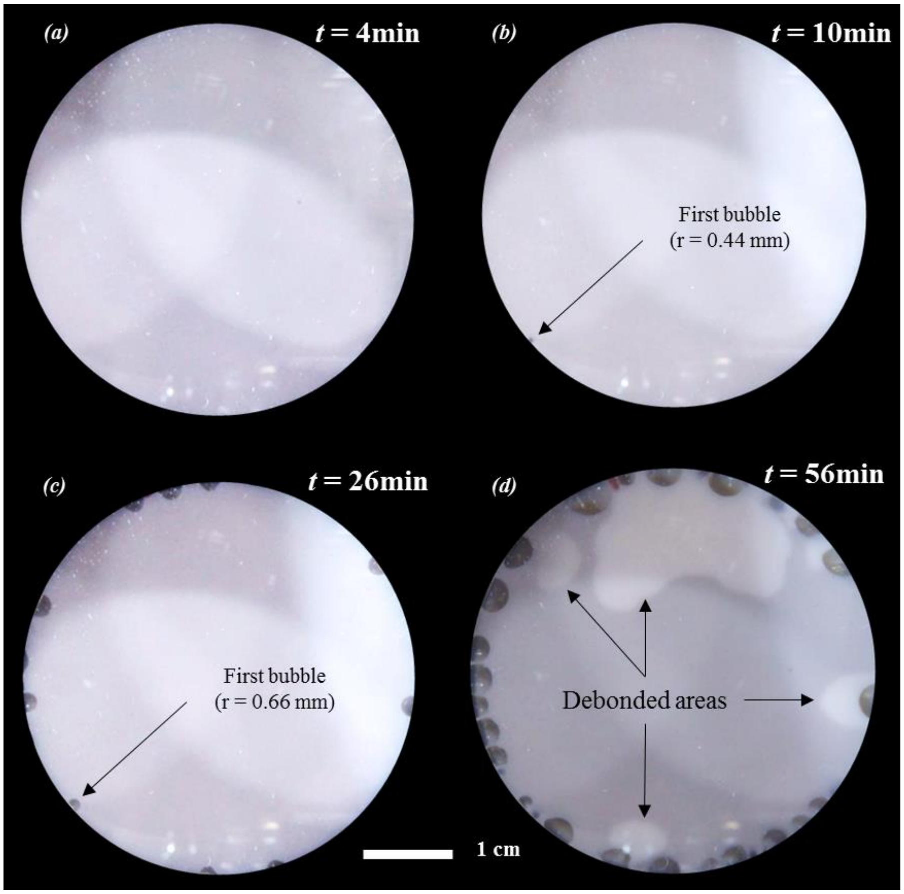

Figure 2. Images of S1 sample showing (a) no visible bubbles at the beginning of curing, (b) the appearing of the first bubble, (c) the porosity nucleation and growing process and (d) the debonding of the sample.

The image analysis method described in section 2.2 was used to compute the volume of porosities at the end of cure. Bubbles were assumed to be quarters of spheres, which was visually validated on cured samples. Using the radius obtained from image analysis on each bubble, the volume of each bubble was calculated with the quarter sphere equation. Summation over all detected bubbles resulted in the total volume of porosities in the sample, which is reported in Figure 3 with respect to the conversion level for samples S1, S2, S5 and S6. The conversion level was calculated from time and temperature using a Kamal-Sourour model [14]. The total volume of porosities at the end of cure varied between 0.9 and 1.3 % of the resin sample volume. This low volume of porosities may not seem critical for molding composite parts, however this is due to the sample conditioning and volume, which will have a higher impact on real composite parts. As observed in Figure 3, the desorption process appears to be an exponential function of cure with no effect of the curing temperature. The VOC starts to be generated at around 20 % of conversion, corresponding to the desorption acceleration, and increases exponentially with cure. The diffusion of the gas molecules is promoted by temperature and so is the bubble growth. Note that the cure rate between 20 % and 80 % of conversion is very high, this period actually takes only 20 minutes while the cure rate from 80 % to 99 % is very slow due to molecular diffusion, taking around 60 minutes. At atmospheric pressure, the total porosity in the injected parts is around 1 % and the porosities are localized at the periphery of the cavity, under the window as seen in Figure 2. The bubble growing process seems to be promoted by the peak of temperature at 60 % of cure due to exothermic reaction. However, when adding fibers to the cavity, their high surface tension promotes nucleation and coalescence of gas molecules will result in higher porosity levels.

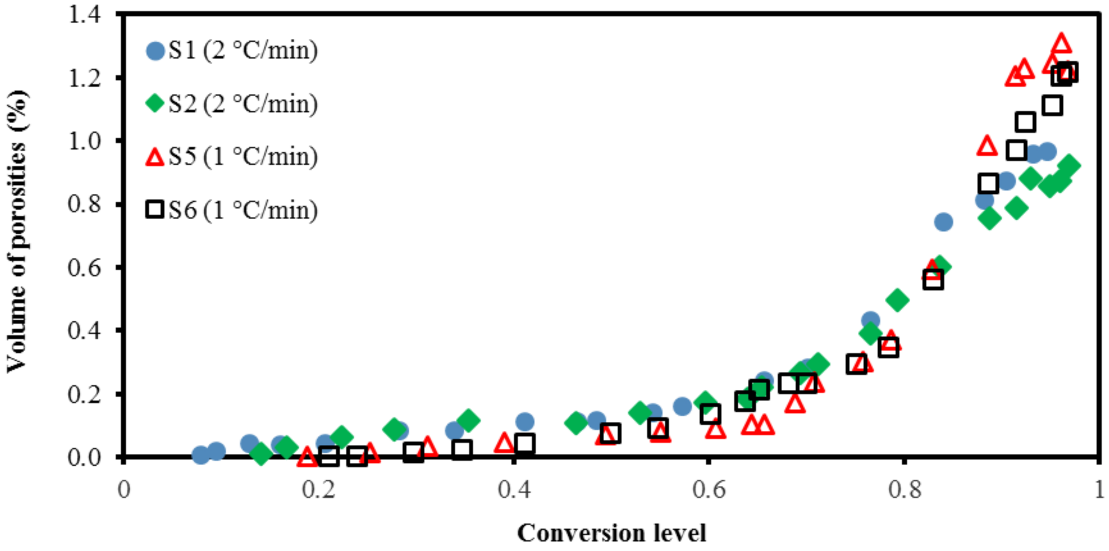

Figure 3. Porosity volume growing with respect to the conversion level of the epoxy resin.

Volatile-induced porosities observed in a composite part are the result of a combination of phenomena such as gas solubility, nucleation and diffusion. Gas solubility is the amount of gas molecules that can be dissolved in a liquid up to a saturation level, which depends on specific conditions as temperature and pressure. Henry [15] defined an empiric law where, at constant temperature in a saturated solution, the maximum concentration of gas can be defined by the following relationship:

$$C_s = H.\, P \tag{1}$$

where C_s is the concentration of gas at saturation, H is Henry's constant and P is the pressure exerted by the gas on the liquid. Consequently, increasing the pressure in the mold should make it possible to dissolve the gases in the resin. For this purpose, three experiments (samples S3, S4 and S7) were devised to study the dissolution of the gas in the resin and the occurrence of irreversibility of desorption process by applying a cyclic consolidation pressure as presented in Figure 4. A pressure from 0 to 345 kPa, was applied periodically every 5 minutes from the beginning of the experiment up to 50 minutes, and then every 3 minutes (see yellow lines in Figure 4). When the consolidation pressure increases above the critical dissolution pressure of the VOC, gas bubbles are redissolved in the liquid resin resulting in a pure resin sample exempt of porosities as observed in Figure 5. While consolidation pressure decreases below the critical dissolution pressure of VOC, gas molecules desorb and diffuse forming visible gas bubbles again. Since this process of desorption and diffusion is closely related to the resin viscosity and so to its conversion level, the capacity of redissolving gas bubbles evolves with the degree of cure. At very high conversion levels, the viscosity is also high so the pressure has little effect on the bubbles or the volatile substances dissolved in the resin. In these three samples, irreversibility was observed at around 93 % of cure. This value seems to match the storage modulus/elastic modulus crossover [14].

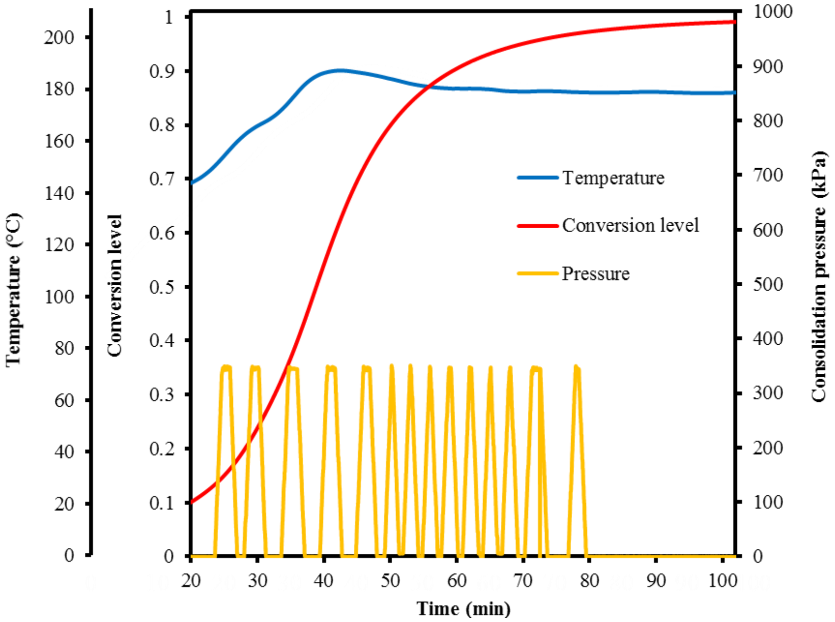

Figure 4. Temperature, conversion level and cyclic pressure in the cavity of the laboratory scale RTM mold.

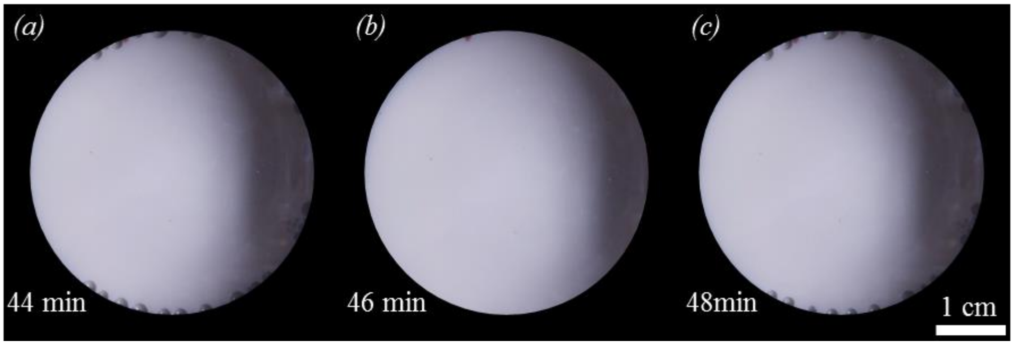

Figure 5. Sample S4 during curing showing (a) visible gas bubbles at atmospheric pressure, (b) no bubbles due to the application of a consolidation pressure and (c) re-nucleation of bubbles due to the release of the consolidation pressure.

4 DIFFUSION MODEL

The proposed mathematical approach is based on the works of Kardos et al. [16], Wood et al. [17] and Ledru et al. [13]. It assumes a bubble of radius R_p trapped in a large volume of liquid resin subjected to a pressure P. The diffusion equation describing the radius bubble evolution with respect to the pressure is defined as follows:

$$\frac{d}{dt}\left(\frac{1}{T}\left(PR_p^3+2\sigma_{LG}R_p^2\right)\right)=\frac{3R_gD}{M_g}\left(C_\infty-C_s\right)R_p\left(1+\frac{R_p}{\sqrt{\pi Dt}}\right) \tag{2}$$

where D is the diffusion coefficient of the chemical species in the resin, M_g is the molecular weight of the gas in the bubble, T the temperature of the system, σ_{LG} the tension surface between the gas and the resin, C_∞ the concentration of gas at the boundary of the considered volume of the resin and C_s is the concentration of gas at saturation defined by equation (1). H was defined by an Arrhenius law [18]:

$$H=H_0\exp\left(\frac{-E_H}{R_gT}\right) \tag{3}$$

where H_0 is a constant and E_d the diffusion activation energy in J.mol^{-1}. D is supposed constant regarding the place in the resin volume in equation (2) but D is a function of the concentration of the mobile species [19]. To take account of those variations of concentration close to the bubble, the diffusion coefficient is defined by an Arrhenius law [18] corrected with a pressure term:

$$D=D_0\exp\left(\frac{-E_D}{R_gT}\right).\left(1+K_p\left(P-P_{atm}\right)\right) \tag{4}$$

where D_0 and K_p are constants, E_d the diffusion activation energy in J.mol^{-1}and P_{atm} the atmospheric pressure. D_0, E_d, H_0, E_H, and K_p have been determined by inverse method from the experimental data.

In Figure 6, numerical results are compared to experimental curing presented in section 2.2. The average bubble radius from experiment S1 was compared to the radius calculated with the diffusion model described by equation (2) for a constant pressure set at atmospheric pressure. The proposed mathematical model predicts the bubble formation and growth with the same trend than the one measured on the experiment. The bubble starts to grow when C_s becomes smaller than C_∞ at around 10 minutes due to the increase of temperature (see equation (3)). As C_∞ stays greater than C_s until the end of curing, the bubble grows until the resin reaches the gel point.

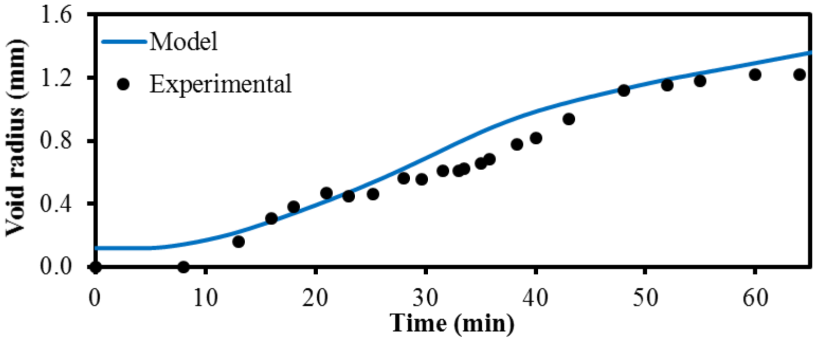

Figure 6. Comparison between the average bubble radius of experiment S1 and the numerical radius (atmospheric pressure).

Results of the predictive diffusion model are presented in Figure 7 and compared to the measured average bubble radius of the experiment S4. When C_∞ is greater than C_s, the resin is oversaturated by the gas and the gas bubble is able to grow in the liquid resin. When pressure increases, there is a volume diminution due to the pressure-volume relation (perfect gas law) and when pressure increases sufficiently, C_s becomes greater than C_∞ and gas molecules diffuse from the bubble to the resin. This leads to a complete dissolution of the gas in the resin. When pressure is released, C_s becomes smaller than C_∞ and the resin goes back into an oversaturated state. The predicted radius with the proposed mathematical model has the same trend and variations than the experimental radius until 48 minutes. This demonstrates that the proposed model can be accurate enough to predict the formation and dissolution of porosities in RTM during molding. The delay observed after 48 min is due to the visco-mechanical effects that have been neglected.

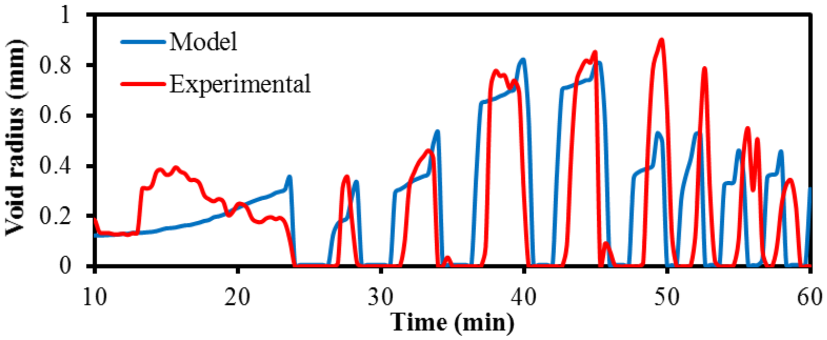

Figure 7. Comparison between the average bubble radius of experiment S4 and the numerical radius (cyclic pressure).

5 CONCLUSION

This work attempts to study void formation occurring on a high temperature epoxy resin during curing that leads to residual porosities in composite parts. Also, this work aims at developing a mathematical model of the void formation. Experiments were carried out on a dedicated mold to observe the formation and dissolution of gas bubbles. This work demonstrates that a high consolidation pressure is not required all along curing process but have to be applied before 93% of conversion level to dissolve remaining gas bubbles in the resin. This pressure has to be kept beyond this conversion level to avoid porosity reformation. If the resin goes through the irreversibility point of 93 % of cure without consolidation pressure, the bubbles due to the gas molecules that had freely nucleated because of the lack of pressure will be trapped in the resin once polymerized.

The diffusion model proposed in this work accounts for the diffusion and solubility phenomenon of VOC during cure. The evolution of the gas bubble radius is due to the variation of the process parameters: time, temperature and pressure, as well as the varying properties of the VOC and the resin. The results of the numerical calculations are in accordance with experimental observations of void formation at atmospheric pressure and with a cyclic pressure. In future, the numerical tool proposed in this work can be coupled with a process modeling tool to bring a very useful solution for the prediction of porosity formation by VOCs.

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