The Effect of Process Parameters on Volatile Release for a Benzoxazine-Epoxy RTM Resin

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Abstract: Volatile release during cure is a potential cause of void formation during the resin transfer molding of complex thermosetting resins. In this study, a blended benzoxazine-epoxy resin system is analyzed to determine the rate at which volatiles are evolved, as well as the dependence of that rate on process parameters. The evolution of thermophysical and thermochemical resin properties is characterized using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The identity and rate of evolution of the gaseous byproducts released during cure are determined at ambient pressure using a Fourier transform infrared spectrometer (FTIR) linked to a reaction cell. The results show that gas release during cure can be reduced but not eliminated by degassing at elevated temperature. Furthermore, the results indicate that the nature and rate of volatile release can be modified by judicious selection of cure cycle, as shown by a preliminary analysis of manufactured neat resin panels.

Key words: Resins, cure behavior, chemical analysis, resin transfer molding

1. INTRODUCTION

Resin transfer molding (RTM) is a closed-mold process traditionally used to manufacture aerospace and automotive composite components with complex geometric features, good surface

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finish, and low porosity. During RTM, microstructural defects can be caused by incomplete resin flow or the entrapment of gaseous species. Flow-induced porosity arises when the infiltrating resin gels before the fiber preform has been fully saturated. Incomplete infiltration may be caused by low preform permeability, high resin viscosity, or an improper selection of gate or vent locations. It may, however, be effectively mitigated by judicious material and process parameter selection and mold design. Gas-induced porosity forms if gas bubbles remain entrapped within the part at the time of resin gelation.

Air-induced voids are the most common, and can be eliminated by degassing the resin prior to injection to remove entrapped or dissolved air, drawing vacuum within the mold cavity during injection, controlling the resin infiltration velocity such that, in conjunction with the preform morphology and permeability, both intra-tow and inter-tow gas entrapment are minimized, and applying sufficient hydrostatic pressure during cure.

Gas-induced voids may also be caused by gaseous by-products of the resin polymerization reaction. However, most traditional RTM resins are formulated to release minimal volatiles during cure. The most common thermoset resins used in RTM, epoxies, are easily processed and exhibit relatively high mechanical properties and chemical/solvent resistance, although their fire/smoke/toxicity (FST) behavior is poor [1]. Phenolic resins have also been used in RTM applications because of excellent FST characteristics and high dimensional stability. However, phenolics are comparatively brittle and have a limited shelf life. Additionally, the synthesis of phenolics often requires the use of harsh acids or bases, which can ultimately increase manufacturing and consumer costs [2,3]. Generally, both materials release few volatiles during

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cure owing to the limited use of solvents during the fabrication of the resin and the reaction chemistry itself [4].

Recently, interest in composite applications involving high temperature and extreme environments has motivated the development of new polymer blends that seek to combine the desirable mechanical and thermal properties of their constituents while mitigating their drawbacks. One such combination consists of a benzoxazine and epoxy blend, which retain epoxy-like solvent resistance and mechanical properties, while exhibiting phenolic-like FST behavior [5,6]. Furthermore, these blends have been shown to be stable at room temperature, exhibit minimal cure shrinkage, along with low moisture uptake under hot and humid conditions [7]. The potential drawback of such systems is a complex chemical cure process, which can consist of both the polymerization/cross-linking of the individual constituents as well as possible interactions. In some cases, the progression of the cure reaction can lead to volatile release during cure, and cause microstructural defects such as bulk and surface porosity.

The benzoxazine/epoxy resin considered in this study can undergo 16% mass loss by volatilization when cured at ambient pressure in a thermogravimetric analyzer (TGA, TA Instruments Q5000 IR). During molding, this offgassing can lead to significant void formation: Figure 1 shows examples of the surface porosity and through-thickness porosity that can occur within RTM samples produced with this resin in certain process conditions, even when no entrapped air bubbles are initially present.

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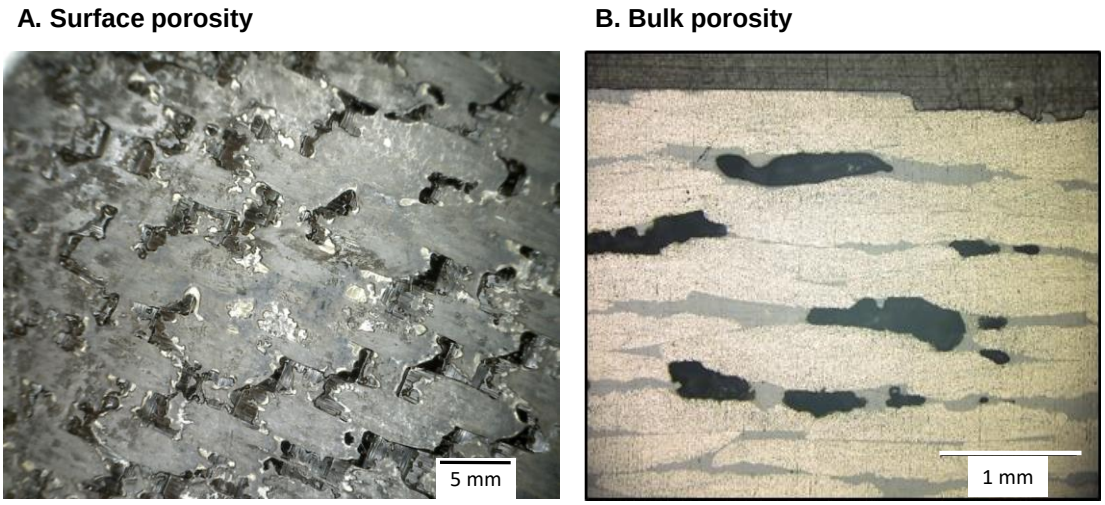

Figure 1: (A) Surface and (B) through-thickness porosity in an RTM sample.

Resin transfer molding has been the subject of research for more than two decades, and a significant body of experimental and modeling literature has been developed [6–12]. However, only limited studies have been carried out on voids induced by volatiles, which may arise well after injection, during hydrostatic cure. This relative scarcity is understandable, as traditionally, little or no weight loss during cure has been one of the requirements for a high-performance RTM resin. For example, resin systems such as epoxies, poly-ether amide resins (PEAR), allyl phenol-formadehyde novolacs (AP), phenyl ethynylphenol-formaldehyde novolac (PEPFN), and bisoxazoline-phenolics are commercial RTM resin types with low-volatilizing behavior [8]. Within liquid molding literature, the issue of volatile release during resin cure has been acknowledged to some extent via the development of specialized RTM tools. Some of these tools allow the withdrawal of volatiles produced during cure [9] using modular inserts that absorb offgases which are subsequently removed [10], while others use a glass window in an effort to observe and tailor the cure cycle to prevent it. In addition, Ghose, Watson et al. [11] concluded that monomer degradation can have a significant effect on final part porosity in a vacuum-assisted

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RTM, but that tailoring the cure cycle can prevent degradation and void formation. This study demonstrates that for such materials, successful processing will rely on effective protocols for reducing defect formation. Such protocols must be in turn derived from a fundamental understanding of the relationships between material properties, process parameters and the rate and identities of volatile released.

The issue of porosity induced by sources other than entrapped air has also been studied in the context of prepreg processing. For example, Grünenfelder and Nutt [12] examined the effect of dissolved moisture on final part porosity in vacuum bag-only processing, showing that the pressure of vaporized water can create exponential increases in void content with cure temperature. Naganuma and co-workers [13] examined the relationship between residual prepreg solvent and voids, showing that residual solvent can drastically affect void topology, and Agius and co-workers [14] showed that cure cycle modifications could decrease void content by up to a third without any effect on the final degree of crosslinking. There has also been extensive modelling of void growth in thermoplastic polymers, as seen in the work by Roychowdhury, Gillespie and Advani [15]. In addition, Hou and Jensen [16] have examined the use of a novel double-vacuum bag method for void reduction when volatilization during cure, whether because of water, solvents, or other reaction byproducts, is a critical concern.

In general, the literature confirms that volatile release during cure complicates defect suppression. In RTM, numerous process adjustments can be used to modify the resin behavior during the degassing and infiltration steps. However, after infiltration is complete and the resin is stationary and curing under hydrostatic pressure, only the cure temperature and pressure are adjustable. As a result, a detailed understanding of the relationships between these process

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parameters, the polymerization reaction of the resin and the nature and rate of volatile release is essential.

In this study, we analyze the factors governing volatile release for a benzoxazine-epoxy blended resin. The cure kinetics of the resin are determined using standard thermochemical methods, while volatile release is characterized using thermogravimetry and Fourier transform infrared spectroscopy (FTIR). The combined data is used to identify predominant influences of volatile release and indicates that volatile release can be mitigated or limited by specific changes to the process conditions. The results provide viable guidelines for defect reduction and process optimization.

2. EXPERIMENTAL DETAILS

The resin selected for this study consists of a benzoxazine-epoxy blend developed specifically for RTM manufacturing. This particular system is a pre-commercial resin formulation, whose chemistry is specifically chosen to emphasize defect formation phenomena such as volatile release. Accordingly, issues such as cure-induced volatilization may be more of a concern than in commercially available resin systems. The system is a low-viscosity, one-part thermoset with a recommended cure cycle consisting of injection at 110°C and three-hour cure at 185°C. The minimum viscosity of the resin is approximately 0.1 Pa·s.

The resin was analyzed in both idealized (non-isothermal or isothermal) and realistic cure conditions using different experimental methods. The resin cure kinetics were measured using differential scanning calorimetry (DSC) in order to track the polymerization/cross-linking process. The resin viscosity was tracked throughout cure using parallel plate rheometric dynamic analysis (RDA). The relationship between cure temperature and volatile release was investigated using a gas-

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phase FTIR spectroscopy system coupled to a large-mass reaction cell. Finally, TGA measurements were performed to determine the mass loss throughout cure. Two sets of conditions were investigated. First, characterization data was obtained during an idealized non-isothermal ramp, isothermal dwell or combined ramp and dwell conditions. Afterwards, realistic cure cycles consisting of both injection and cure dwells were used to simulate realistic thermal conditions. Tables 1 and 2 summarize the characterization experiments, and each method is described in detail as following.

Table 1: Summary of all characterization experiments performed. "R" and "D" designate ramps and dwells, respectively

Type	*Degassed*	*Cure Type*	*Ramp Rate (°C/min)*	*Nominal Dwell Time (min)*	*Cure Temp (°C)*
TGA	Yes	R + D	1, 2, 3	120	175, 185, 195
TGA	No	R + D	2	60	185
TGA	No	R	1, 2, 3, 5, 10		
TGA	No	D		60	165, 175, 185, 195, 205
DSC	No	R	1, 2, 3, 5, 10		
DSC	No	D	--	360	165, 175, 185, 195, 205
Cell/FTIR	No	R + D	1, 3	60	220
Rheology	No	R + D	1, 3	120	220

Table 2: Summary of all realistic cure cycle experiments performed. "R" and "D" designate ramps a dwells, respectively

Type	*Degassed*	*Cure Type*	*Ramp Rate (°C/min)*	*Dwell Temp (°C)*	*Dwell Time (h)*	*Cure Temp (°C)*
Cell/FTIR	Yes	R+D+R+D	2	110	1	175, 185, 195
Cell/FTIR	Yes	R+D+R+D	2	130	1	185
Rheology	Yes	R+D+R+D	2	110	1	175, 185, 195
Rheology	Yes	R+D+R+D	2	130	3	185

Resin de-gassing.

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When desired, 20 mL samples of the resin were degassed in a 50 mL beaker within a vacuum oven (Yamato LDP21) at 110°C and approxximately 10.1 kPa (0.1 atm). As described in later sections, a small subset of FTIR characterization experiments was carried out on non-degassed resin in order to maximize signal intensity. Subsequently, TGA, RDA, and FTIR analyses were performed on degassed resin using realistic cure cycles to simulate industrial processes. In addition, a separate TGA experiment was conducted to measure the difference in mass loss between degassed and non-degassed resin.

Cure Kinetics - Differential Scanning Calorimetry.

The heat of reaction at elevated temperatures was measured in calorimetric DSC experiments (TA Instruments Q2000). Neat resin samples weighing approximately 10 mg were placed in sealed hermetic aluminum pans. Non-isothermal scans were performed at rates of 1, 2, 3, 5, and 10 ˚C/min from 35˚C to 315˚C, and isothermal runs were performed at 10˚C increments between 165˚C and 205˚C. After each isothermal run, a non-isothermal scan at 2˚C/min from 35˚C to 315˚C was performed to measure any residual heat release. The non-isothermal scans were used to determine the maximum heat of reaction, while the isothermal runs were used to estimate the thermodynamically allowable maximum degree of cure possible at a given cure temperature.

Mass Loss - Thermogravimetric Analysis.

Mass loss experiments were carried out by TGA (TA Instruments Q5000 TGA). The temperature was ramped from 25°C to 175, 185, or 195°C at 1, 2, 3°C per minute and held isothermally for 90 min until there was no further change in mass loss. These cure temperatures and ramp rates were chosen because they were small changes from the manufacturer's recommended cure cycle. In addition to these experiments, the manufacturer's recommended cure cycle, consisting

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of a one hour injection dwell at 110°C followed by a 2°C/min ramp to an isothermal 185°C hold for 3 hours, was also performed for samples of degassed and non-degassed resin. The TGA was purged with nitrogen at a rate of 50 mL/min throughout all tests to prevent condensation of volatiles within the furnace.

Volatile Release - Fourier Transform Infrared Spectroscopy.

FTIR analysis was performed on the gas phase volatiles released during cure. Resin samples weighing approximately 10 g were cured within a heated reaction cell (Advise Sensing) (Figure 2) connected to a gas-phase FTIR (Thermo Electron Nicolet 4700). The amounts used in the reaction cell are orders of magnitude greater than in typical TGA-FTIR samples, allowing for greater signal-to-noise ratios and unambiguous identification of evolved species. The control software within the reaction cell maintained the temperature to within 1°C of the set temperature, while nitrogen gas swept the volatiles from the reaction cell headspace into the FTIR. A mass flow controller (Alicat Scientific) maintained a constant carrier gas flow rate of 5 mL/min (± 0.02 mL/min), as measured at 25˚C.

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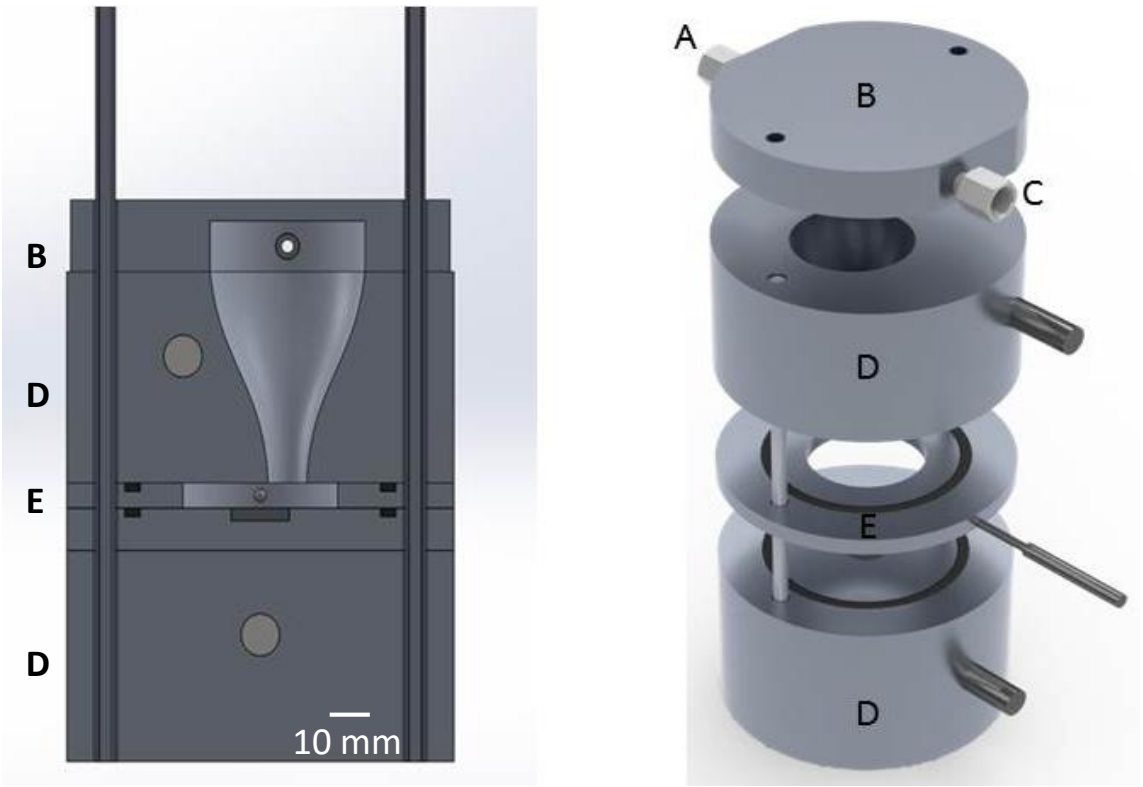

Figure 2: Cross-section view of reaction cell assembled (left) and exploded view of reaction cell assembly (right) showing (A) N_2 carrier gas inlet, (B) reaction cell fitting, (C) connection to FTIR, (D) heating blocks with attached heating rods, and (E) sample holder with attached thermocouple.

The FTIR was equipped with a HgCdTe detector as well as a multi-pass spectroscopic absorption gas cell (TGA/IR Interface, Thermo Electron) designed to detect and analyze low-concentration vapor products. The spectroscopic absorption cell was maintained at 240°C to prevent volatile condensation within the system. Note that in these experiments, the resin is exposed to ambient pressure, rather than to the higher pressures used during actual molding. As such, the volatile release behavior represents a worst-case scenario. However, in this manner, we can detect all volatile species released, assess the relative amounts, and develop suppression conditions.

While the DSC experiments clarify the cure reaction of the resin, the FTIR experiments were used to identify the volatile species being released throughout cure, and to determine relative intensity. Consequently, the effects of specific cure cycle characteristics were studied. Non-isothermal ramps

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were performed at 1 - 3°C per minute, as well as realistic cure cycles of various ramps and dwells. A summary of FTIR experiments performed are provided in Tables 1 and 2.

Rheology

Resin viscosities were used to determine gel and vitrification times by RDA using a rheometer (TA Instruments ARES 2000EX) outfitted with 40 mm bottom plates and 25 mm top plates, separated by a gap of 1 mm. Tests were carried out at 0.10% strain with a frequency of 1 Hz within the linear viscoelastic regime. The rheology experiments are summarized in Tables 1 and 2. RTM Instrumentation. Neat resin panels were produced at appropriate temperatures and pressures, as described in the volatile analysis section. These panels were produced in an instrumented, lab-scale RTM mold that afforded accurate control of temperatures and pressures, unlike typical RTM molds used for part production in the composites industry. The purpose of these experiments was to confirm the conditions for volatile suppression developed in the previous section. In both experiments, we used a ramp rate of 2°C/min to 185°C with an intermediate, one-hour injection dwell at 110°C.

3. RESULTS AND DISCUSSION

Cure Kinetics and Viscosity.

Figure 3A shows results from the non-isothermal DSC experiments. The evolution of the heat of reaction exhibited a traditional single-peak specific heat flow curve for all studied conditions. The total heat of reaction, HT, was obtained by integrating the area under the exothermal peak and dividing by the sample mass. The final results of the calculations are shown in Table 3. The average HT from the non-isothermal scans was calculated to be 448.9 J/g ± 7.2 J/g. The heats of reaction from isothermal runs are provided in Table 3, and data plotted in Figure 3B. The total heats of

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reaction indicate that with lower temperature dwells, the resin cured only partially. However, the total heats of reaction obtained by summing the dwell and residual components are consistent to within 1% with results from non-isothermal scans.

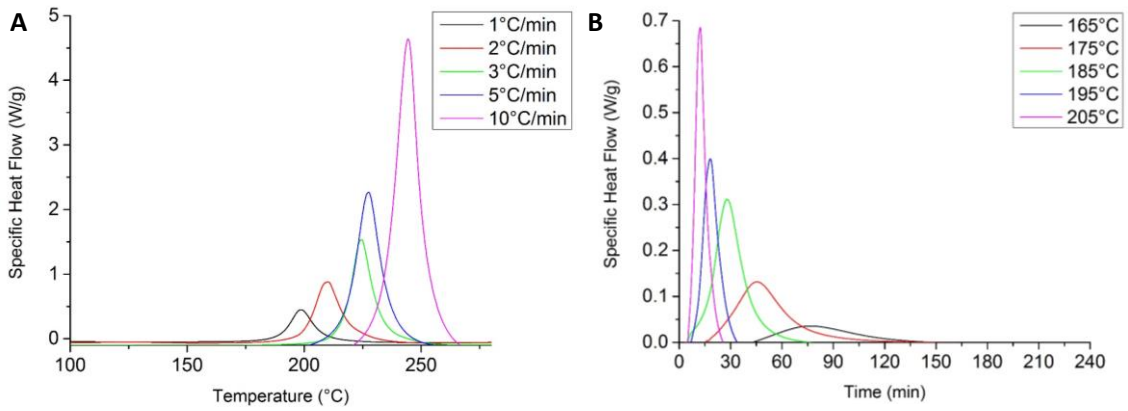

Figure 3: (A) Exotherms versus temperature from non-isothermal scans. (B) Exotherms versus time from isothermal runs.

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Table 3: Total heats of reaction for non-isothermal scans (left) and specific exotherm energies for isothermal runs (right)

Non-Isothermal DSC Scans		*Isothermal DSC Runs*			
Ramp Rate	H_T	*Temp.*	*Heat of Reaction*	*Residual amount*	*Total Heat*
1°C/min	451.6 J/g	165°C	363.6 J/g	83.28 J/g	446.88 J/g
2°C/min	459.6 J/g	175°C	400.5 J/g	43.02 J/g	443.52 J/g
3°C/min	447.0 J/g	185°C	438.6 J/g	15.15 J/g	453.75 J/g
5°C/min	440.2 J/g	195°C	448.4 J/g	10.14 J/g	458.54 J/g
10°C/min	445.9 J/g	205°C	449.8 J/g	6.39 J/g	456.19 J/g

The relatively consistent values obtained for the total heat of reaction indicates that despite the presence of multiple thermosetting constituents within the blended resin, the nature of the polymerization/cross-linking process is largely independent of cure cycle. Furthermore, the presence of a single heat of reaction peak indicates that the primary constituents of the resin combine in a single reaction, or react independently but simultaneously.

The degree of cure (α) can be defined from the heat of reaction using Eqs. (1) and (2), and is shown in Figure 4. This figure suggests that the resin is more sensitive to dwell temperature changes at lower temperatures rather than at higher temperatures.

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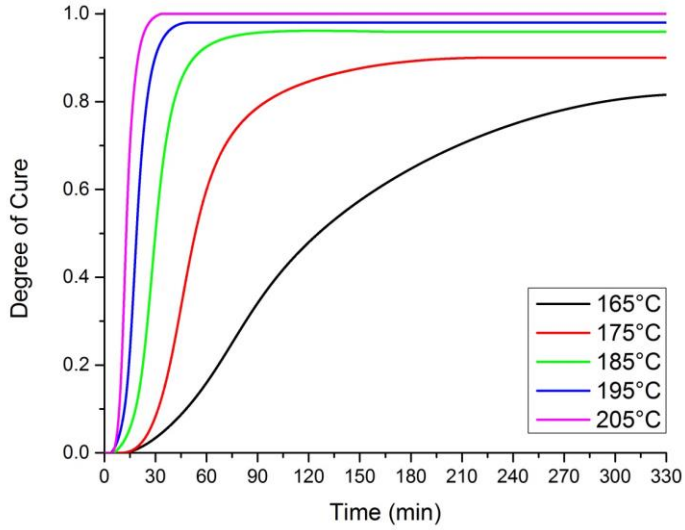

Figure 4: Degree of cure evolution versus time for various cure dwell temperatures

$$\frac{d\alpha}{dt} = \frac{1}{H_T}\frac{dH}{dt} \qquad \textbf{1}$$

$$\alpha = \frac{1}{H_T}\int_0^t \left(\frac{dH}{dt}\right) dt \qquad \textbf{2}$$

Rheometer data was analyzed to determine gelation and vitrification times. Gelation was selected as the crossover between G' and G" [17] and vitrification was defined as the post-gelation tan delta (tan δ = G'/G") peak [18]. Specific results will be discussed in the context of volatile release.

Thermogravimetric Analysis.

The total mass loss as a function of degree of cure for both isothermal and non-isothermal experiments is shown in Figure 5. For non-isothermal experiments, larger amounts of volatile release were observed for lower ramp rate s. Conversely, for isothermal experiments, the mass loss was more consistent, with 13 to 14% mass loss observed in all experiments with no degradation observed up to 350°C. The decrease in total mass loss at high ramp rates may be a consequence of

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reaction kinetics – at higher ramp rates, the rapidly increasing degree of cure and viscosity "lock in" solvents and other potential volatiles, preventing evolution, bubble nucleation and migration towards the free surface of the sample. Because isothermal dwells at higher temperatures are associated with faster cure, this data suggests that greater instantaneous rate of mass loss should be observed for higher cure temperatures.

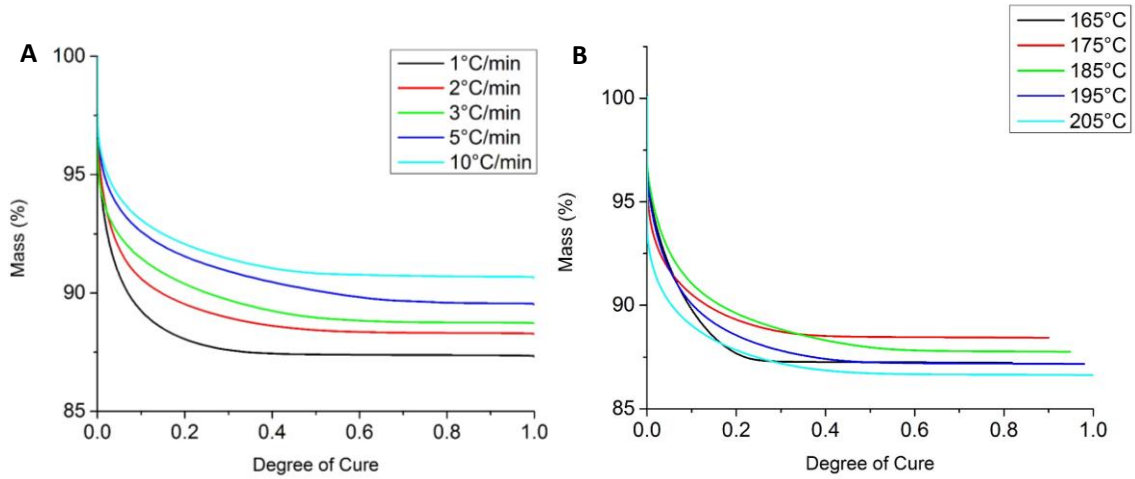

Figure 5: Mass loss data versus degree of cure, as seen in the TGA for (A) non-isothermal ramps and, (B) isothermal dwells

For cure cycles consisting of a ramp and hold, the ramp rate and cure temperature are summarized in Figure 6. At ambient pressure without degassing, volatile release is consistent and independent of cure cycle, with all samples exhibiting between 13% and 16% mass loss. This constancy is due to the cure reaction being dominated by the isothermal cure hold, rather than the non-isothermal ramp. When the resin is degassed (1 h at 110°C, 0.1 atm), volatile release is reduced by approximately 2%, as shown in Figure 7. The consistent mass loss behavior indicates that the mass loss is either concurrent with or caused by the resin cure process; consequently, typical methods of pre-processing may not be wholly applicable to this system.

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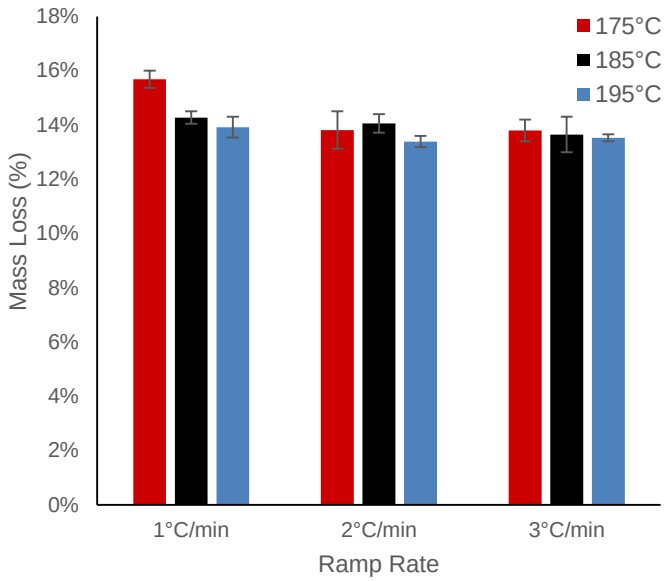

Figure 6: Total mass loss versus ramp rate for degassed samples

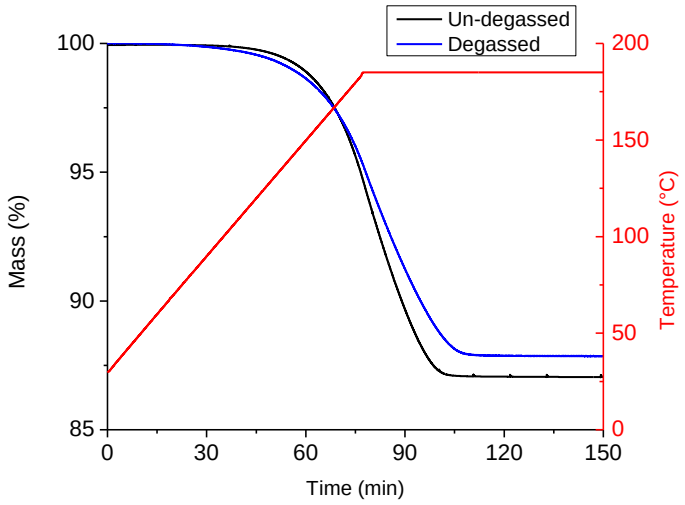

Figure 7: Comparison of degassed versus non-degassed resin

Volatile Analysis and Identification.

Figure 8 shows FTIR spectral data from the reaction cell experiments for a 1°C, 2°C and 3°C per minute ramp to a 220°C hold until cure, along with the cell temperature. To maximize the FTIR signal, the resin in these experiments was not degassed. The color intensity map within the contour

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plots indicates the FTIR signal intensity in unit-less "absorbance units," and is an indicator of instantaneous volatile concentration. The dashed line in Figure 8 indicates gelation and the solid line vitrification, as determined from the RDA experiments. The comparison of FTIR and rheology data clarifies the relationship between viscosity and volatilization. Peak volatilization occurs prior to gelation, but gas release does not cease until vitrification, when the molecular mobility of the polymer chains approach zero. These results indicate that volatile-induced defects could potentially form until vitrification.

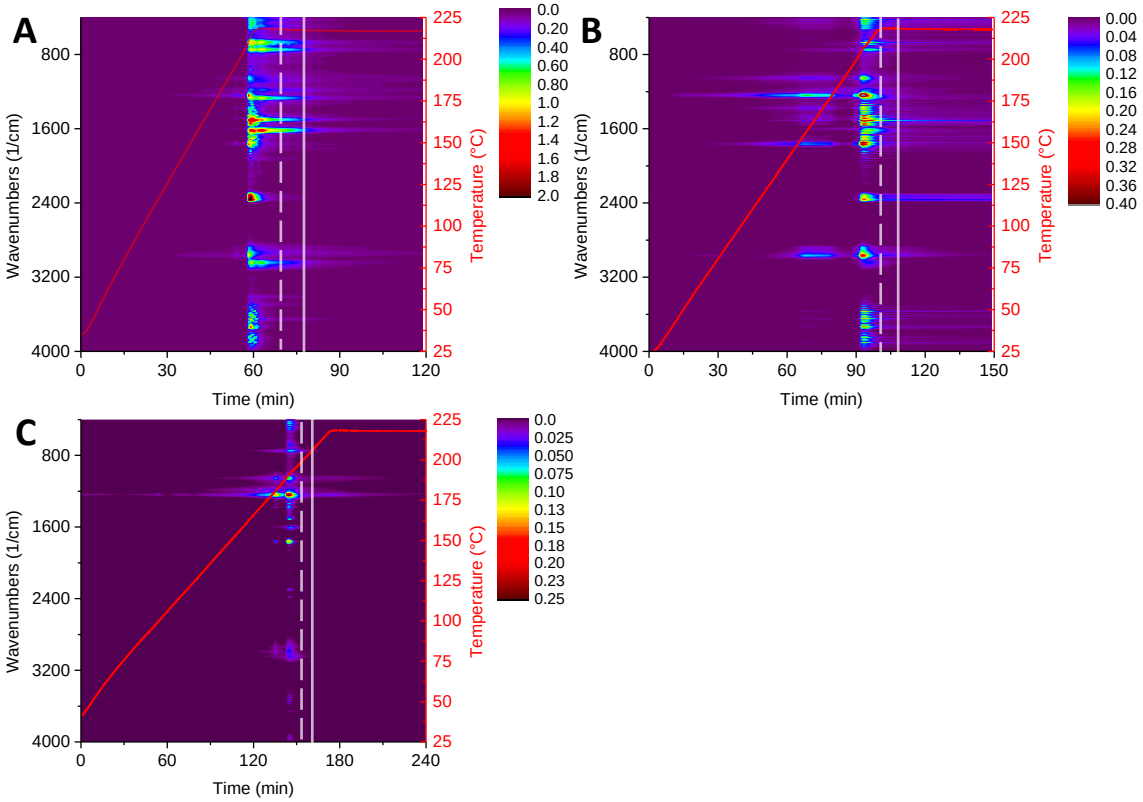

Figure 8: FTIR data for (A) 3°C/min ramp to 220°C and hold, (B) 2°C/min ramp to 220°C and hold, and (C) 1°C/min ramp to 220°C and hold. The intensity of the color scale is in absorbance units. The dashed line indicates gelation and the solid line vitrification

The peak absorbance value in Figure 8A indicates that the maximum instantaneous volatile intensity (which corresponds to the volume- of volatiles within the FTIR) during the 3°C/min ramp

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was an order of magnitude greater than during the 1°C/min ramp. This difference is explained by the DSC data in Figure 3A, which shows that the cure reaction occurs at a slower rate, and thus over a longer time span, when a slower ramp rate is used. The FTIR analysis thus confirms that volatile release is concurrent with resin cure.

The FTIR data also provides insight into the volatile species released during cure. In our analysis, we define onset of volatile release as the point when the absorbance of a particular species exceeds 0.025, which is the signal-to-noise threshold of our detector. In Figure 8A, the onset of ethyl acetate volatilization occurs at 30 minutes (105°C) as indicated by the C-H alkyl stretch (2870 wavenumbers), a C=O stretch (1750 wavenumbers), and C-O stretches (1250 and 1055 wavenumbers). Subsequently, carbon dioxide evolves at 210°C (58 minutes) as indicated by the spike at 2350 wavenumbers, which indicates C=O asymmetric stretching. At the same time, water appears. Finally, the evolution of aniline occurs during the latter half of the 220°C hold, indicated by absorbencies at 1280, 3360 and 3442 wavenumbers, corresponding to the bending and stretching of C-N and N-H bonds, in addition to the absorbencies at 760 wavenumbers, corresponding to N-H bond wagging. Because aniline evolves at high temperatures well after vitrification, it may involve thermochemical phenomena unrelated to cure. Indeed, studies have shown that aniline is a degradation byproduct associated with benzoxazines [19]. Table 4 summarizes the species identified by FTIR, along with the onset times and temperatures during the 3°C/min ramp and hold.

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Table 4: Potential volatiles emitted during the realistic cure cycles and their methods of elimination. Experimental parameters for realistic cure cycles and characterization experiments are listed in Tables 1 and 2.

Species name	*Range of Evolution*	*Condition Observed*	*Boiling Point*	P^{vap} *at Onset*	*Elimination Method*
Isohexane	60-110°C	Realistic cure Characterization	69°C	0.75 atm [22]	Mold Pressure
Ethyl acetate	60-Gel	Realistic cure Characterization	77°C	0.55 atm [23]	Mold Pressure
Phenol	170-185°C	Realistic cure	182°C	0.83 atm [24]	Mold Pressure
Water	190-200°C	Characterization	100°C	>> 10 atm [25]	Degassing
Carbon dioxide	190-200°C	Characterization	-57°C	>> 10 atm [26]	Degassing
Aniline	> 200°C	Characterization	185°C	1.98 atm [27]	Temp. Control

When the resin cure cycle is modified, the volatilization behavior changes accordingly. During the 1°C/min ramp and hold shown in Figure 8C, the evolution of ethyl acetate begins earlier (at 85°C rather than at 105°C). Additionally, the peak absorbance is much lower – 0.25 in the 1°C/min ramp-and-hold - versus 2.0 in the 3°C/min ramp-and-hold. Finally, as shown in Figure 8B, the results of the 2°C/min ramp is an intermediate between the 1°C/min and the 3°C/min ramp-and-hold. This is evidenced by the maximum absorbance and time-frame in which the volatiles are emitted during cure. Superimposing the 3°C/min and 1°C/min FTIR data on the DSC data, as shown in Figure 9, supports the assertion that volatile release is related to cure cycle, but also shows that secondary effects may exist. For the 3°C/min ramp-and-hold, the dα/dt peak occurs near the peak volatile intensity, whereas in the 1°C/min ramp-and-hold, the same peak appears ~15 min later. These observations indicate that transient volatile release behavior can be affected by the cure cycle.

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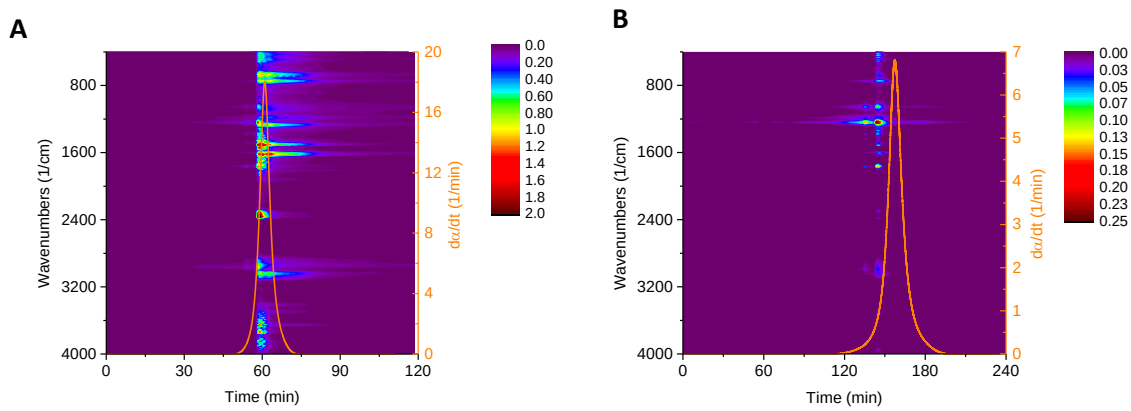

Figure 9: FTIR data with DSC cure rate data superimposed for (A) 3°C/min ramp and (B) 1°C/min ramp to 220°C. The intensity of the color scale in in absorbance units.

The hydrostatic resin pressures achieved in a closed RTM mold can potentially suppress certain volatiles. However, among the species detected using FTIR, the water and carbon dioxide are problematic, because their vapor pressures at evolution exceed 1 MPa (10 atm), and therefore might require high-pressure RTM processing. As a result, volatile mitigation may require additional strategies. In the next section, we investigate the influence of degassing and selection of cure cycle on the identity, amount, and rate of released volatiles.

Realistic Cure Cycle Analysis.

Experiments consisting of single ramps or isothermal holds provide useful insights into basic material behavior. However, in practice, cure cycles generally include both ramps and dwells. Here, we analyze four cure cycles representative of typical manufacturing practice. The first is based on a standard cure cycle (ramp from room temperature at 2°C/min to 110°C, hold for one hour, ramp at 2°C/min to 185°C and hold until fully cured). The second and third cycles differ in the cure temperature (dwells at 175°C and 195°C), while the fourth consists of a modified injection dwell (injection dwell for 3 hours at 130°C rather than 110°C, and cure dwell at 185°C). The ramp rate of 2°C/min was selected due to the high sensitivity and specificity of volatiles from our previous set of

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characterization experiments. Prior to each cycle considered, the resin is degassed for 30 minutes at 110°C, at an absolute pressure of 10.1 kPa (0.1 atm).

Figure 10 shows that for all four cure cycles, the maximum absorbance values decreased relative to the 1°C/min and 3°C/min ramp to 220°C, but volatiles were not completely eliminated. The hypothesis that the rate of volatile generation depends directly on the rate of cure is supported in this experiment, as the maximum FTIR signal intensity decreased with lower dwell temperature (and thus lower cure rate). Additionally, the release of aniline is eliminated because the cure temperature does not exceed 185°C, and with degassing, the presence of carbon dioxide and water are completely eliminated. Indeed, the sudden spike at 2400 wavenumbers disappears, as do the peaks at 1280, 3360 and 3442 wavenumbers. Because of the high vapor pressure of both water and carbon dioxide, eliminating these species is potentially critical for suppressing volatile-induced porosity. Additionally, removal of aniline to avoid degradation is equally important for producing high quality parts [19].

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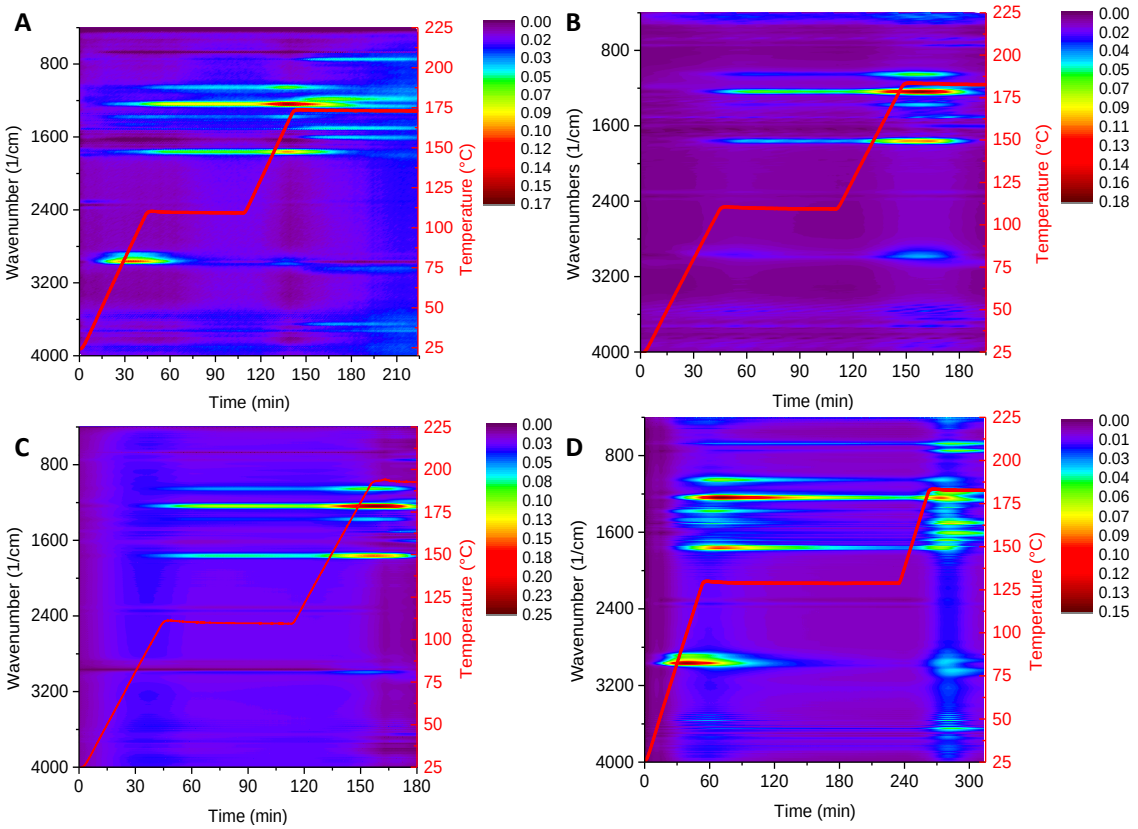

Figure 10: FTIR data from the reaction cell showing volatile release as a function of cure temperature for various cure cycles. Cure dwell at: (A) 175°C, (B) 185°C, (C) 195°C, (D) Injection dwell for 3 hours at 130°C. The intensity of the color scale in in absorbance units.

When the cure temperature is reduced from 185°C to 175°C, two additional species are visible in the FTIR trace – isohexane, which appears at the beginning of the cure cycle and corresponds to an absorbance at 3000 wavenumbers (C-H bond), and phenol, which appears at 150 minutes, corresponding to the three absorbance bands at 750, 1500, and 1600 wavenumbers. From additional tests, isohexane appears to be a byproduct of the release agent (Frekote 770-NC), and appears in FTIR spectra intermittently, only after the release agent is freshly applied in the reaction cell. The appearance of phenol only in lower-temperature cure dwells, coupled with the shift in peak volatilization from well into the dwell at 185°C to the end of the ramp at 175°C, indicates that the

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release of volatiles can be path dependent with respect to the cure cycle. However, the nature and consequences of these volatile shifts on final part quality requires an additional study in the future. The FTIR data for the 3-hour dwell at 130°C indicate that volatiles evolve during two periods. The first occurs at the start of the injection dwell as the temperature reaches 130°C. The second arises during the cure dwell, and is less pronounced than in previous cycles. The presence of phenol, previously observed only in the 175°C dwell, is also observed here, indicating that both the identity and the release rate of the volatiles are affected by temperature and temperature history.

The temperatures of evolution and the boiling point and vapor pressures (Pvap) of the various species at the onset of evolution detected during cure, along with the experimental conditions in which they were observed, are shown in Table 4. Amongst these, the carbon dioxide and water species have the highest vapor pressures at the temperature of evolution, but these species can be eliminated using degassing and appropriate cure cycle selection. The vapor pressures of the volatiles that could not be eliminated via degassing or cure cycle changes, particularly ethyl acetate, phenol and isohexane, can suggest the minimum pressure that must be applied to suppress volatile-induced porosity. While the actual combination of species released during molding and the resulting void nucleation and growth phenomena are not yet fully understood, process modifications that mitigate the release of high pressure volatiles will decrease the total void-generating potential, as well as reduce the resin pressure required to suppress volatiles.

RTM Instrumentation.

To confirm these conclusions, neat resin panels measuring 7.62 cm by 12.7 cm by 0.32 cm (3 inches × 5 inches × 1/8th inch) were cured in a lab-scale RTM mold featuring a transparent mold wall. The resin was degassed for 30 min at 110°C and injected at the same temperature into a

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vacuum-evacuated mold cavity. The mold was flushed with resin until no entrapped air bubbles remained within the cavity. Then, the resin outlet was sealed, and two realistic cure cycles were imposed, consisting of a 2°C/min heat-up ramp to 110°C, a one-hour hold at 110°C, and a 2°C/min ramp to 170°C or 185°C, respectively. Two cure pressures were used for each dwell temperature: 0 kPa and 103 kPa (gauge) at 185°C, and 0 kPa and 69 kPa (gauge) at 170°C.

Cure pressure selection was not arbitrary, but was guided by Antoine's equation [20]. 103 kPa and 69 kPa are the vapor pressures of the highest volatilizing species at each cure temperature, 185°C and 170°C respectively. Because the vapor pressure is defined as the pressure exerted by the gaseous species on its surrounding medium, the hydrostatic pressure of the resin required to collapse each bubble must be greater than or equal to the vapor pressure. Experimental observations (including those in Figure 11) indicate that the critical pressure required to produce bubble-free neat resin panels is approximately equal to the vapor pressure of the highest volatilizing species. Note that this agreement does not necessarily imply that the vapor pressure is a direct indicator of whether void formation can be suppressed, as void nucleation and growth are complex phenomena that depend on multiple material properties and process factors. However, because the vapor pressure of the volatile species is a significant driver of void nucleation, this semi-quantitative analysis shows that it can be used as a first-order approximation.

Photographs of both panels are shown in Figure 11. The neat resin plates cured at atmospheric pressure exhibited substantial porosity. While the morphologies of the bubbles formed at 170°C differed from those formed at 185°C owing to the voids having time to coalesce, in both cases substantial amounts of volatiles were generated during cure, indicating insufficient hydrostatic pressure. Conversely, the panel cured at higher pressure exhibited no porosity, indicating that void

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nucleation and growth were effectively suppressed. This experiment confirms that cure-induced volatilization can be limited with proper process modifications, and validates the utility of the characterization methodology used in this work.

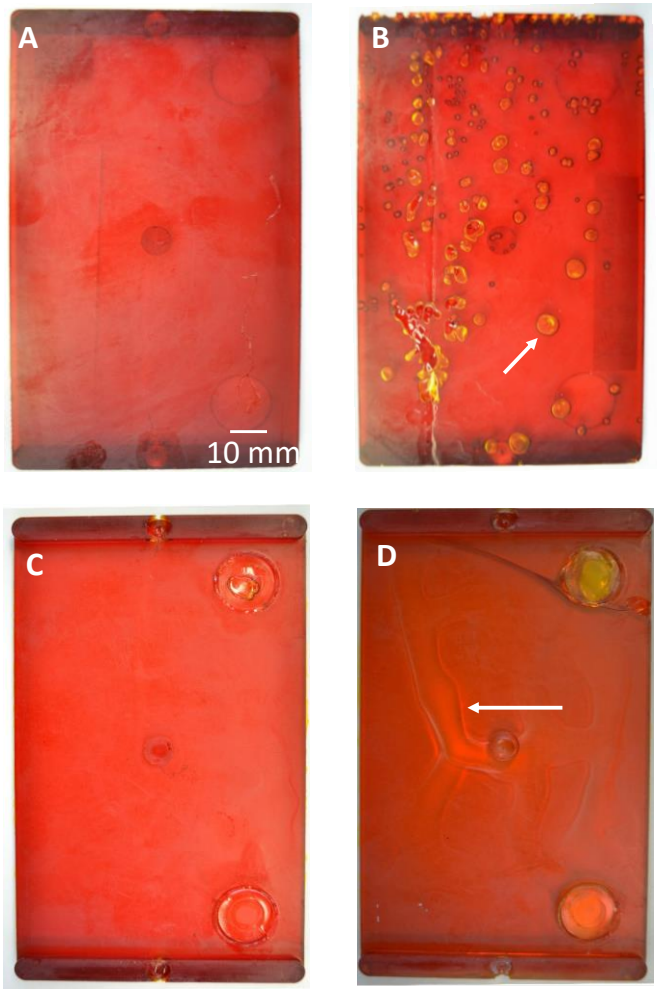

Figure 11: Neat resin panels cured at: a) 185°C and 103 kPa of pressure, b) 185°C and atmospheric pressure, c) 170°C and 69 kPa, d) 170°C and atmospheric pressure.

4. CONCLUSIONS

We have investigated the relationships between the resin cure reaction and the release of volatile gases for a blended benzoxazine-epoxy RTM resin. DSC experiments were performed to determine the bulk degree-of-cure and rate of cure as functions of time and temperature. In addition, TGA and

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an FTIR spectrometer coupled to a heated reaction cell provided insights into the identity of volatiles and the volatile release behavior of the resin as functions of both cure cycle and degree of cure. These methods produced complementary datasets and elucidated the polymerization reaction and the effect of process parameters on volatile release rates.

The results indicate that for resin blends such as the one selected, the identity and rate of release of volatiles can be tailored by judicious selection and control of cure cycle, and degassing prior to cure. These process modifications can reduce the driving forces behind defect formation in the manufacture of composite parts by decreasing the instantaneous rate of volatile nucleation and growth, and process modifications based on them were shown to inhibit void formation during the RTM processing of four neat resin plates.

All characterization experiments within this study were conducted at ambient pressures (because of instrument capabilities) and consequently represent a worst-case scenario in which all evolved gasses are present. In an RTM mold, high applied pressures can dissolve some evolved gasses and suppress void growth, as well as potentially influence the cure reaction itself. A clearer understanding of these phenomena is desirable and is the subject of a companion paper [21]. In this study, we also did not account for the role of other defect-forming phenomena, such as entrapped air, inadequate fiber wetting, or cure shrinkage. Such factors could potentially interact with volatile release, further complicating defect suppression, and require further study. Nevertheless, an accurate understanding of basic resin properties and behavior during cure is a necessary first step, and can guide process development and contribute to manufacturing guidelines for successful and efficient manufacture of high-quality composite parts.

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