Method for in situ analysis of volatiles generated during cure of composites

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Abstract: Conventional epoxies used in composites are formulated to release minimal amounts of volatiles during cure, aside from moisture, which is a perpetual concern. However, a variety of polymers are used in production of composite parts, including adhesives, prepregs, and non-epoxy polymers, and sources of volatilization during processing can be both difficult to determine and problematic. Here we demonstrate a general method for in situ analysis of volatile release during cure. The method improves upon traditional characterization techniques of TGA/MS and TGA/FTIR (thermogravimetric analysis, mass spectroscopy, and Fourier transform infra-red spectroscopy). We characterize a commercial epoxy prepreg typical of those used in aerospace, a benzoxazine/epoxy blended liquid resin intended for high-temperature service, and finally, a high-temperature polyimide. By understanding the identity, origin, and kinetics of volatile release in these three materials, we can prescribe additional pre-treatments and define process windows to minimize and even eliminate volatile-induced porosity. Finally, we demonstrate the utility of the reaction cell/FTIR approach for characterizing cure-induced volatiles and mitigating final part porosity.

Key words: Processing monitoring; Cure behaviour; Chemical analysis; Porosity

1. INTRODUCTION

In composites manufacturing, volatile release during cure in any molding environment can be problematic. While traditional epoxies such as bisphenol A (DGEBA) or tetraglycidal

diaminodiphenyl methane (TGDDM) are designed to release little or no volatiles during cure, studies have shown that moisture release in epoxy prepregs can be a source of porosity in composite parts [1], [2], [3]. Other polymers, particularly those formulated for high temperature service, such as benzoxazine and polyimides, generally include solvent additions and complex chemistries which have been shown to generate volatiles during cure [4], [5].

Regardless of the origin, unmitigated volatile release in both open- and closed-molding environments has been shown to cause porosity in the final manufactured part, ultimately decreasing performance and material properties [1], [5], [6]. Additionally, understanding both the kinetics and the identity of the volatiles released is essential to develop and implement mitigation strategies, which will depend on when during cure the volatiles are generated (i.e., pre- or post-gelation). For example, high vapor pressure volatiles that evolve pre-gelation can be removed via degassing, while volatiles that are generated post-gelation can be suppressed by judicious temperature control [5]. These possibilities dictate a need for an in situ method to analyze the volatiles generated during cure [7].

Current strategies for characterizing cure-induced volatiles in situ rely on conventional analytical tools. These tools typically include a thermogravimetric analyzer coupled with a mass spectrometer (TGA/MS), or a thermogravimetric analyzer coupled with a Fourier transform infrared spectrometer (TGA/FTIR). Yet these techniques are both limited in scope and utility. The applicability of a mass spectrometer generally depends on the particular instrument configuration, although typical mass spectrometers struggle with identifying mixtures [8], [9]. A mass spectrometer determines the mass-to-charge ratio (m/z) of a particular molecular fragment, then works backwards to piece the fragments together. When mass spectrometry is applied to mixtures, analysis is complicated by the fact that the resulting m/z is generally a convolution of all components in the mixture. While mass

spectrometry can provide valuable insight on the molecular weight of a volatilized species, m/z ratios do not reveal direct information about particular chemical bonds or structures, and thus can be less useful than FTIR spectra for identification of compounds. While the inclusion of a gas chromatograph (GC) before a mass spectrometer can be useful to aid in the separation of mixtures for easier identification, this approach carries the potential for oversaturation of the GC column, and precludes in situ identification of volatiles.

A TGA/FTIR setup is similar to the TGA/MS technique, although samples used in TGA/FTIR are generally small ($\sim$50 mg), and the low signal-to-noise ratios in spectra often make detection/identification of trace volatiles impossible [10]. Here, we describe how this limitation can be overcome by replacing the TGA with a reaction cell (RC) that accommodates larger samples ($\sim$10 g samples versus $\sim$50 mg samples). Larger sample sizes generate much greater signal-to-noise ratios in FTIR spectra and enable definitive identification of trace volatile species. Furthermore, the RC can be operated under conditions that replicate actual composite processing conditions, including high temperature and pressure. These conditions cannot easily be achieved in a standard TGA without risking instrument damage. For these reasons, the method we will describe has some distinct advantages over conventional techniques for in situ volatile characterization.

In this paper, we consider four resin systems commonly encountered in composite processing: (a) a conventional epoxy prepreg used for aerospace applications, (b) a liquid benzoxazine/epoxy resin designed for RTM processing, and (c) two forms of a high-temperature polyimide. These systems were selected to demonstrate the broad utility and versatility of the reaction cell/FTIR technique (RC/FTIR) for the various material types commonly used in composite manufacturing, along with the range of temperature and pressure conditions that the technique can be used to

replicate. We outline how the method can be employed to develop strategies for volatile mitigation, techniques for material handling, and processing steps to reduce cure-induced volatilization.

2. MATERIALS and METHODS

Five resin systems were selected for analysis of volatiles released during cure. The resins were selected as case studies to represent the variety of forms, temperature/pressure ranges, processing routes, and types of polymers encountered in the production of composites. The first resin system was a commercial epoxy prepreg (Cycom 5320-1, Solvay) designed for out-of-autoclave (OoA), vacuum-bag only cure. The cure cycle was 177 °C for 2 h. Prior to analysis, the prepreg was conditioned for 24 h at 90% relative humidity and 23 °C (±1°C).

The second resin system was an amine-cured, low-flow, toughened epoxy resin system designed for primary aircraft structures and helicopters (HexPly 8552S plain weave, Hexcel). During the manufacture of this particular resin system, there was residual solvent remaining in the final product. The cure cycle was a 5 °C/min ramp to 177 °C followed by a 2-hour dwell at ambient pressure.

The third resin was a benzoxazine-epoxy blended resin designed for liquid molding by RTM (resin transfer molding). The thermoset resin featured a low-viscosity, one-part liquid formulation with a recommended process cycle of injection at 110 °C and a three-hour cure at 185 °C. Because this resin is intended for use in molding processes where pressure is a key processing parameter, volatile analysis was performed by curing at two applied pressures: 101 and 206 kPa (14.7 and 30 psi absolute).

The final resin system selected was a high-temperature polyimide resin (TriA-X, Kaneka) for compression molding of prepreg. The cure cycle consisted of a dwell at 250 °C for four hours to allow for imidization, removal of residual solvent, and crystallization, followed by an intermediate dwell at 325 °C for 30 min, and a cure dwell at 371 °C for two hours. Volatile characterization

experiments were performed on the polyimide neat resin (resin system 4), as well as the polyimide prepreg (resin system 5). In both sets, the same cure cycle was used.

The experimental setup (Fig. 1) for in situ analysis of gaseous volatiles released during cure consisted of a heated reaction cell (Advise Sensing) connected to a gas-phase FTIR spectrometer (Thermo Electron Nicolet 4700). The reaction cell (RC) consisted of a sample cavity (50 mm in diameter by 10 mm in height) that could be heated to 400 °C and pressurized to 450 kPa. A carrier gas (typically nitrogen) carried evolved volatiles to an FTIR spectrometer via a heated gas line. Note that the amounts used in the RC (~1–10 g with a recommended minimum sample size of 500 mg, depending on rate of volatile release) were orders of magnitude greater than typical TGA-FTIR samples (~50 mg), yielding greater quantities of volatiles that boosted signal-to-noise ratios in FTIR spectra and unambiguous identification of evolved species. The control software within the RC maintained the temperature to within 1 °C of the set temperature. In addition, the order-of-magnitude difference between the sample size and the size of the reaction cell heaters ensured uniformity of sample temperature. 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. In a control experiment with acetone, nominal detection times from onset of vaporization to detection averaged ~5 s. A more complete validation of this technique is reported elsewhere [5].
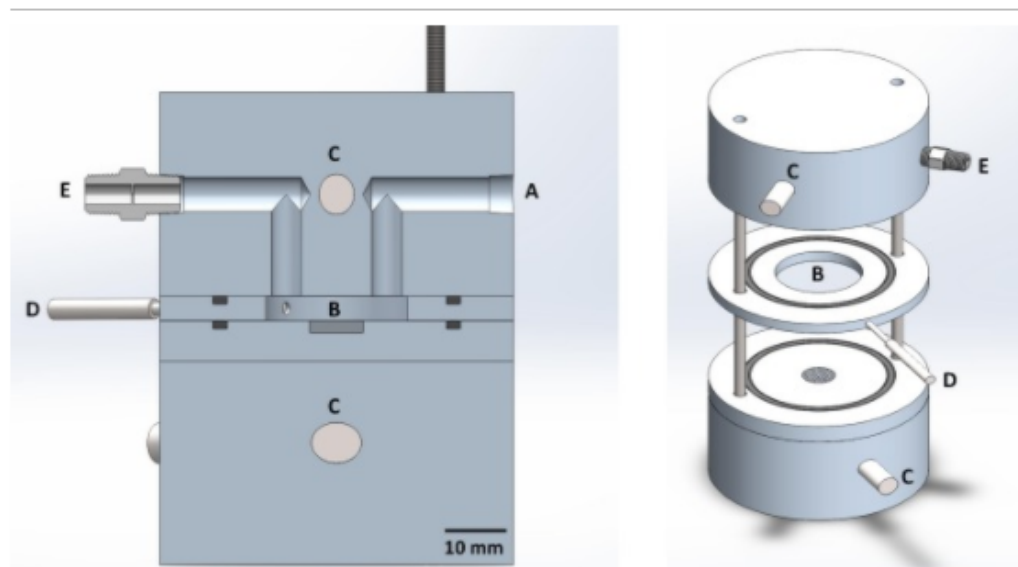
Fig. 1. (A, left) Cross section view of a reaction cell (RC), showing (A) inlet port (B) sample compartment (C) heaters (D) control thermocouple (E) outlet port to FTIR. (B, right) Expanded view of the reaction cell. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The purpose of the mass flow controller was to control flow through the spectrometer. If the flow rate was too high, the signal intensity within the spectrometer would be too low for accurate identification of the volatiles. However, a flow rate that was too low would oversaturate the detector and risk instrument damage. For our setup, a flow rate of 5 mL/min was suitable to allow for clear and accurate identification of the evolved gaseous species without risking detector oversaturation. For pressurized experiments, the mass flow controller was connected downstream of the FTIR, allowing for equal and uniform pressure to be applied across the entire system, while allowing for flow of the volatiles through the instrument.

The FTIR was equipped with a HgCdTe detector and a multi-pass spectroscopic absorption gas cell (TGA/IR Interface, Thermo Electron) designed to detect and analyze low-concentration vapor species. In all experiments, the Gram-Schmidt intensity, which represents the total spectroscopic

absorbance within the cell, was collected in addition to the interferograms. The spectroscopic absorption cell was maintained 20 °C above the RC temperature to prevent volatile condensation within the system. For analyses of the polyimide, a high-temperature gas cell (TGC-M-LV from Harrick Scientific), equipped with silver O-rings (Parker Hannifin) and a temperature controller (ATC-024-2, Harrick Scientific) was used to achieve the high temperatures required. The resin systems, experimental conditions, and FTIR setup are summarized in Table 1.

Table 1. Resin systems considered.

Resin system	Sample Size (g)	Pressures (kPa, abs)	FTIR Accessory
Benzoxazine resin	~10	101, 206	TGA/IR interface
Epoxy prepreg	~10	101	TGA/IR interface
Hexcel 8552S prepreg		101	High temperature cell
Polyimide resin	~0.75	101	High temperature cell
Polyimide prepreg (1-ply)	~1.25	101	High temperature cell
Polyimide prepreg (3-ply)	~1.25	101	High temperature cell

As needed, mass loss experiments were also carried out by TGA (TA Instruments Q5000 TGA) to complement the spectroscopic data from FTIR with quantitative weight loss data. Like the RC experiments, the manufacturer's recommended cure cycle was used to define the temperature profile. In all experiments, the TGA was purged with nitrogen flow (50 mL/min) to prevent condensation of volatiles within the furnace.

3. RESULTS

3.1. Resin system 1: benzoxazine/epoxy blend

Fig. 2A shows the spectroscopic trace generated from a benzoxazine/epoxy blend characterized via TGA/FTIR following the manufacturer's recommended cure cycle (RCC). However, the signal intensity for the majority of the cure cycle was below the signal-to-noise ratio of the instrument, even when using the maximum sample size allowable within the TGA. The exception was during the period 120–150 min, where 3 faint signals appeared at 1250, 1730, and 1750 wavenumbers, corresponding to CO and CO bonds. However, the identification of these bonds was insufficient to clearly identify the gaseous species evolved during cure, as the presence of these bonds are ubiquitous in nature.
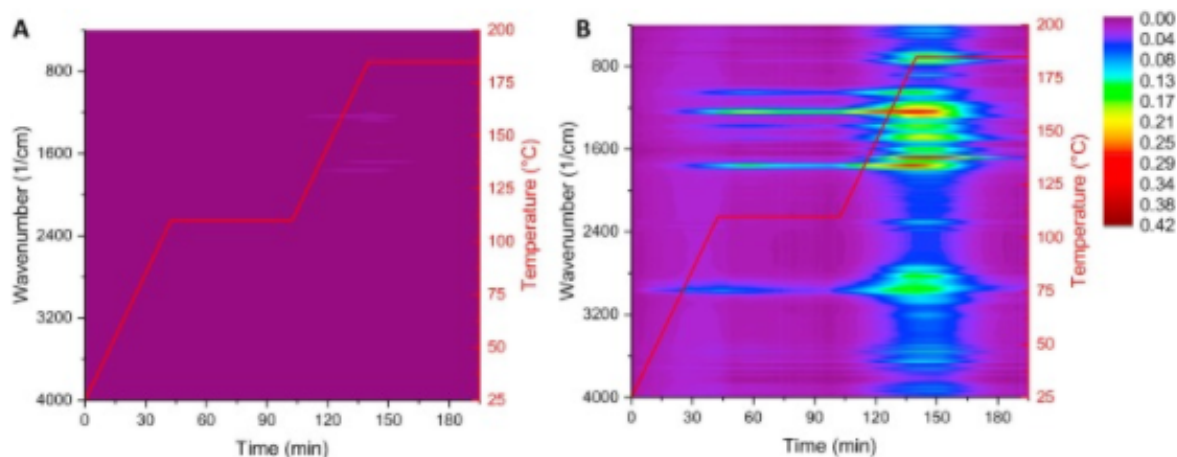
Fig. 2. Comparison of a (A) ∼50 mg TGA/FTIR sample and a (B) ∼10 g RC/FTIR sample. The same intensity scale is used for both figures. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

In contrast, Fig. 2B shows spectroscopic traces generated from a benzoxazine/epoxy blend (liquid) at ambient pressure cured within the RC/FTIR. Following the same recommended cure cycle, three major species were detected: (a) ethyl acetate (as indicated by the C—H alkyl stretch at 2870 wavenumbers, a C═O stretch at 1750 wavenumbers, and C-O stretches at 1250 and 1055 wavenumbers), (b) hexanes (C—H bond stretching at 3000 wavenumbers), and (c) phenol (para-substituted out-of-plane bending at 850 wavenumbers, aromatic C — C stretch at 1500 wavenumbers, and O—H bond stretching at 3400 wavenumbers) [11]. Note that liquid molding of benzoxazine/epoxy blends requires addition of a solvent, which in this case was ethyl acetate, and hexane is a constituent of common mold release compounds. By identifying the temperatures at which these species evolve, the approximate pressures required to suppress volatilization can be readily calculated via Antoine's equation [5], [12].

Application of pressure can suffice to suppress the evolution of gaseous species that would otherwise volatilize from the polymer solution. This effect is manifest in Fig. 3, in which the volatile characterization experiment in Fig. 2B is repeated, but under positive pressure (206 kPa (abs)). The modest applied pressure almost completely suppresses the volatiles, and only trace amounts of gaseous species are detected in the FTIR spectrum. In similar fashion, positive pressure can be applied during composite processing to likewise suppress volatile evolution. For example, Fig. 4A shows a benzoxazine-epoxy composite cured under pressure (206 kPa abs) using the manufacturer's recommended cure cycle. The sample shows no porosity. In contrast, a similar sample cured at atmospheric pressure shows extensive porosity (Fig. 4B).
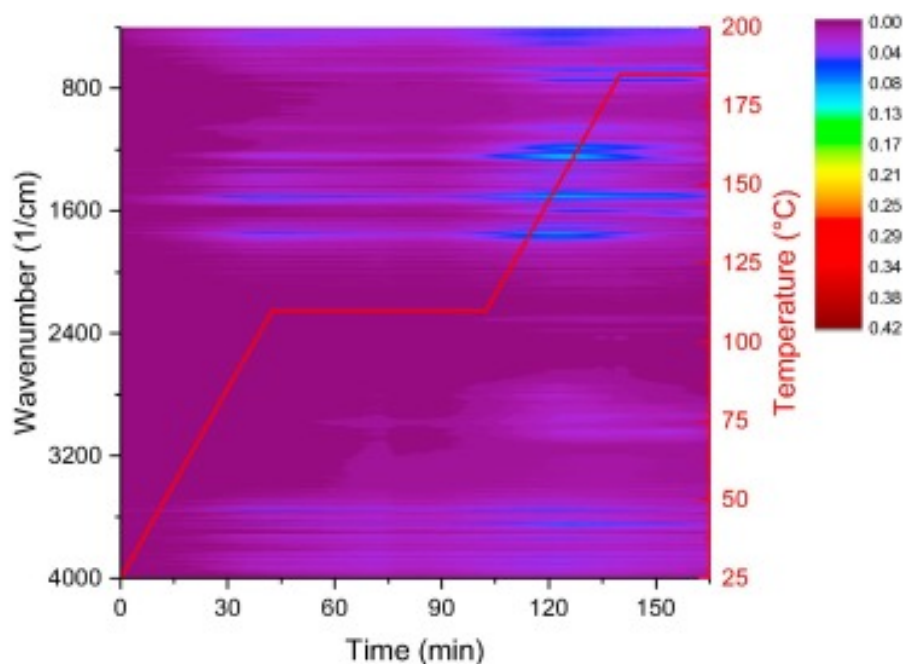
Fig. 3. Spectroscopic trace for a benzoxazine/epoxy sample at 206 kPa (abs). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
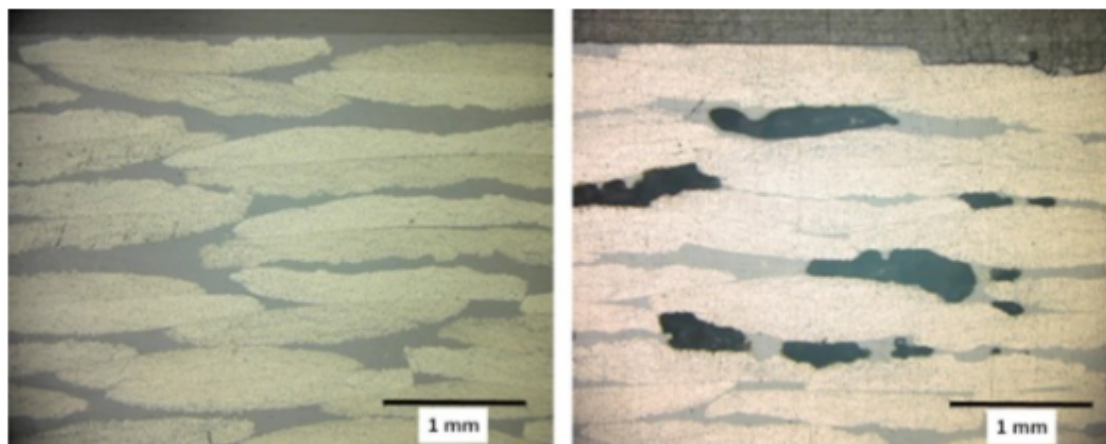

Fig. 4. Cross-section of a benzoxazine/epoxy composite part cured under (A) 206 kPa (abs) and (B) 101 kPa (abs) with the same temperature profile as in Fig. 3. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

In reality, void nucleation, bubble growth, and the solubility of gasses within a reacting medium are complex and multi-faceted phenomena. Bubble growth can depend strongly on material

properties, processing conditions, and other factors. However, because vapor pressure is a significant driver for void nucleation, one can use vapor pressure as a first-order indicator to determine if bubble nucleation will occur at any time within a particular process window [13], [14]. In addition, if experiments using the RC/FTIR to simulate process conditions indicate that volatilizing species cannot be suppressed by application of pressure alone, one can design/prescribe pre-treatments, such as degassing or temperature control, and/or modified cure cycles, to suppress the volatilization of these species [15]. Further discussion on analysis of volatile release in the context of process induced defects has been reported [5].

3.2. Resin system 2: epoxy pre-preg

Fig. 5 shows time-resolved FTIR spectral data generated during cure of an epoxy prepreg that had been previously conditioned at 90% RH for 24 h. After conditioning, the epoxy was fully saturated and gained ~0.2% mass [1]. The temperature profile imposed is overlaid (red curve), and the color intensity map indicates the instantaneous volatile concentration within the spectrometer, with high absorbance levels depicted in red/orange. Volatiles are detected starting at ~30 min, and the concentrations peak at ~45 min. The spectroscopic data indicate that the primary volatile species produced during cure was water, as expected, and that water release occurred primarily 30–60 min into the cycle [11].
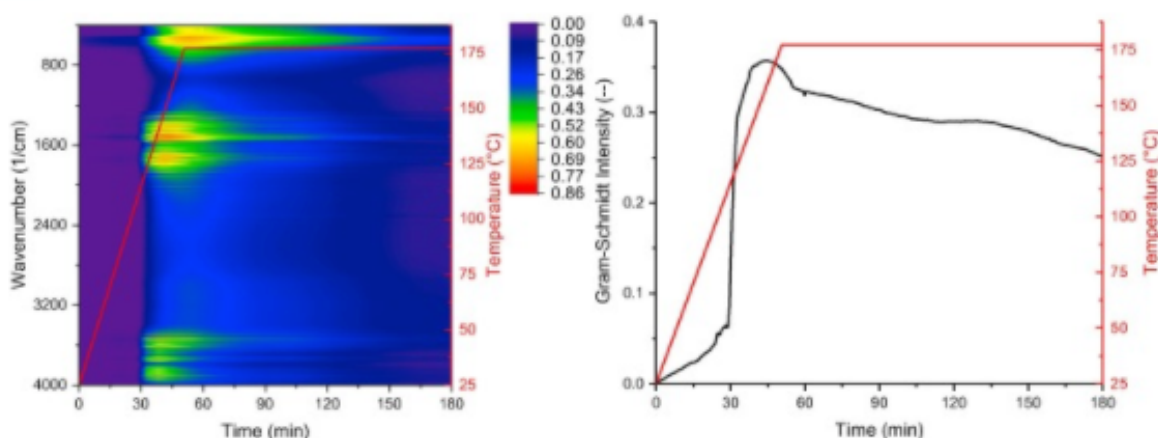
Fig. 5. (A) Spectroscopic trace for an epoxy prepreg sample. (B) Gram-Schmidt trace of the spectroscopic intensity for an epoxy prepreg sample. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 5B shows the Gram-Schmidt intensity corresponding to Fig. 5A. The Gram-Schmidt intensity provides the total absorbance within the FTIR gas cell, which can be correlated to the instantaneous concentration of volatiles within the cell. The correlation is achieved by considering the total amount of light being absorbed by the sample, as opposed to light at an arbitrary wavenumber. Thus, the Gram-Schmidt intensity curve effectively provides a "comprehensive summary" of the spectroscopic waveform data at any given point in time [16]. In addition, the Gram-Schmidt intensity curve can be integrated and compared to quantitative Fischer titration data to obtain both the kinetics of moisture release, as well as a quantitative measure (grams) of total moisture release from the sample [17], [18]. In Fig. 5B, the maximum rate of volatile release occurs at ~40 min, coincident with the intensity maxima. At this point, the cell reaches 100 °C, and moisture is being released. Afterwards, there is a slow decay in signal intensity, although the non-zero intensity indicates that moisture is still evolving from the prepreg sample, even when the cell temperature reaches 177 °C.

Note that in Fig. 5B, the peak in spectral intensity arises after the cell reaches 100 °C because of the attractive bond between water and epoxy molecules within the prepreg. Absent such an attractive force, water would no longer be present after the cell reached 100 °C. Water and epoxy molecules are bound by hydrogen bonding, and thus water can be difficult to remove, even under vacuum and at temperatures >100 °C. Furthermore, applied pressures can be required to suppress moisture-induced porosity in prepregs due to the high vapor pressure of water at cure temperatures [1]. These observations support the widespread practice of limiting humidity exposure during handling of prepregs. Even small quantities of moisture can result in unacceptable porosity levels because of the large volume expansion of the vapor phase. Thus, it is important to control and restrict prepreg exposure to humidity during the manufacturing process to limit moisture uptake [1], [19].

Also, previous work has shown that with large/contoured parts, the pathways for volatile escape become increasingly tortuous, making it more difficult to remove dissolved moisture. However, the RC/FTIR setup can be used to replicate manufacturing conditions (temperature and pressure) and to perform process/cure cycle optimization on a lab scale. In addition, manufacturing challenges such as the evolution of solvents from a prepreg can be detected in situ and thus guide efforts to optimize cure cycles. An example of evolution of solvents from a prepreg is described for resin system 5 below.

3.3. Resin system 3: 8552S pre-preg

Fig. 6A shows the spectroscopic trace generated when a sample of Hexcel 8552S pre-preg is cured within the RC/FTIR. When the RCC was followed, two major species were detected: (a) methyl ethyl ketone (broad H—C=O stretch at 3000 wavenumbers, sharp ketone C=O stretch at 1750 wavenumbers, and alpha beta-unsaturated aldehyde at 1700 wavenumbers), and (b) acetone

(distinctive ketone C$=$O stretch at 1750 wavenumbers and C$-$H methyl stretch at 1260 and 1380 wavenumbers). These are both low boiling solvents, which indicates that they potentially be removed during pre-processing. However, it also means that any trace amounts of these solvents remaining during the cure process will ultimately result in cure-induced porosity.
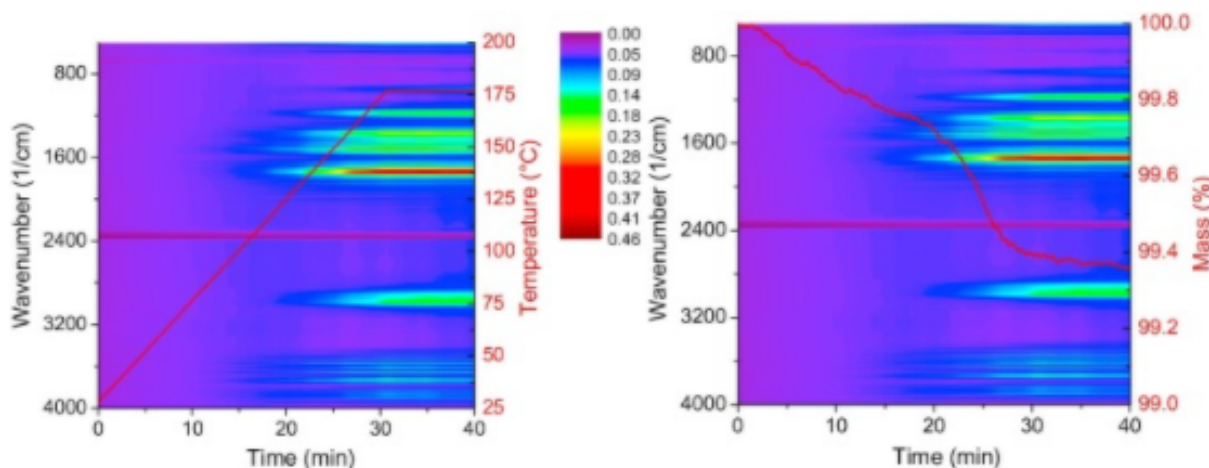

Fig. 6. Spectroscopic trace for a solvated epoxy pre-preg sample cured within the reaction cell (RC) with the superimposed (A) temperature trace (B) mass loss trace.

Fig. 6B shows the spectroscopic trace superimposed onto a TGA mass loss data set, showing that onset of weight loss begins during the ramp and before the cure dwell. Because the onset of cure-induced weight loss occurs before the cure dwell, a judicious cure cycle must be selected in order to suppress cure-induced volatilization and eliminate porosity in the final composite part. However, as studies have shown [20], elimination of volatilization both before cure (via degassing or pre-cure dwells) or during cure is still difficult for this pre-preg. As reported in studies examining co-cure of honeycomb core sandwich structures with the 8552S pre-preg, managing the outgassing of solvents during cure is challenging. Volatile evolution due to gas entrapment or solvents can yield unacceptable amounts of porosity, ultimately leading to poor mechanical properties in the final manufactured part. While strategies such as vented sandwich structures can be used to reduce or

eliminate volatile evolution, these may not always be feasible. An alternative possibility is to use a reaction cell to quantify volatile release, and identify strategies to mitigate solvents during synthesis; subsequently, cure cycle optimization studies can later be applied to eliminate cure-induced porosity altogether. An example of this is shown in the next two resin systems, and has been explored in more detail in a separate study [21].

3.4. Resin system 4: polyimide neat resin

Fig. 7 shows FTIR traces generated from a polyimide powder sample cured at ambient pressure, and demonstrates how the RC/FTIR system replicated the cure cycle required for polyimide consolidation and cure. (The spectroscopic trace shown in Fig. 7 represents the entire cure cycle, which is overlaid on the spectral data.) Because of the large disparity between the quantities of gasses evolved during the first 90 min and the subsequent cure ramps, the data are displayed in the subsequent figure with different color scales (Fig. 8A and B) for clarity. During the first 90 min of cure, the primary volatiles generated are ethanol (OH stretch at 3400 wavenumbers, CH stretch at 3000 wavenumbers, and CO stretching at 1100 and 1050 wavenumbers) and acetaldehyde (similar to the ethanol spectrum, with the inclusion of a small aldehyde peak at 3500 wavenumbers) [11], [22]. The significance of these results is two-fold. First, the volatilization of acetaldehyde is notable, as it is a group 1 carcinogen and poses health and safety risks [23]. Industrial-scale processing of this particular formulation of polyimide would require safety measures to mitigate these risks. Secondly, the evolution of sulfur dioxide (SO bond doublet peak at 1380 wavenumbers) and carbon dioxide (CO doublet at 2200 wavenumbers) is detected during the two subsequent dwells at 350 °C and 371 °C [11]. The polymer formulation does not contain sulfur molecules by design, but these results were consistent over two replicates, introducing the possibility of a residual contaminant acquired during synthesis of the polyimide monomers [24].
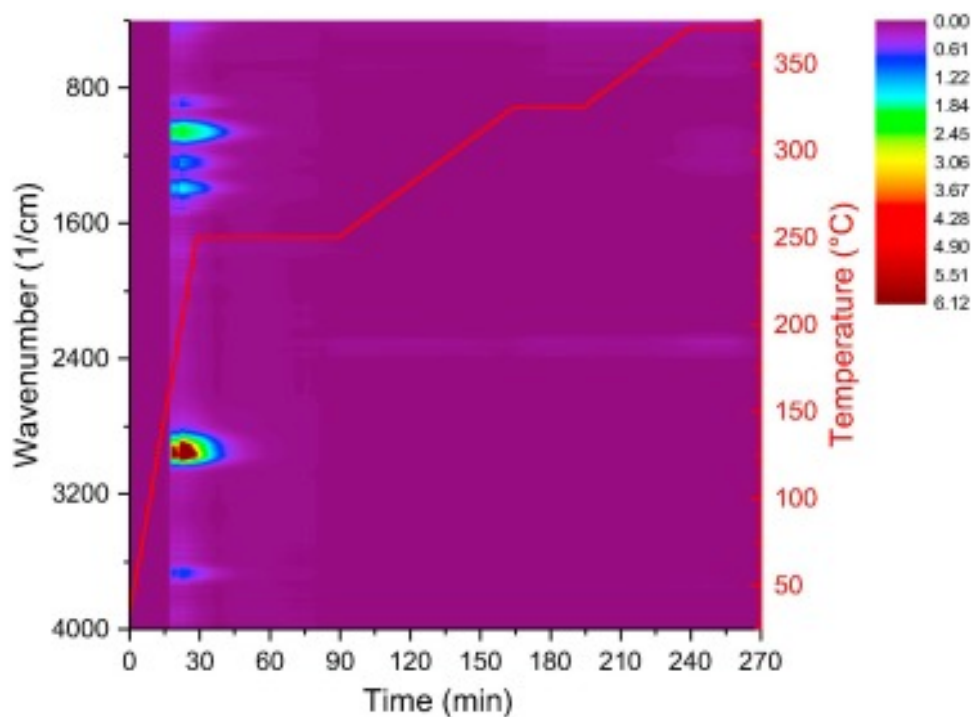
Fig. 7. Spectroscopic traces for a polyimide resin cured within the RC. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
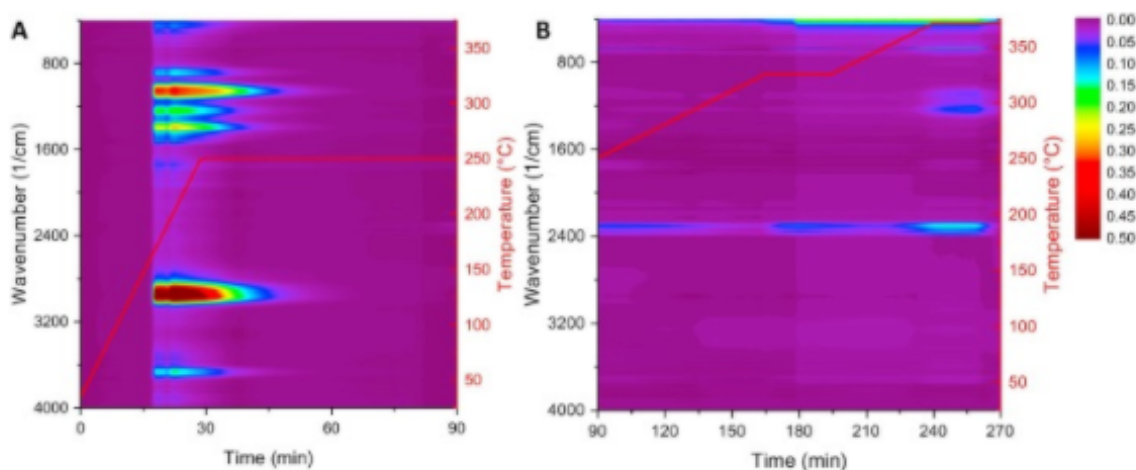

Fig. 8. (A) Spectroscopic traces for the first 90 min of a polyimide resin cured within the RC. Refer to (A) for intensity scale. (B) Spectroscopic traces for the last 180 min of a polyimide resin cured within the RC. Note that the intensity scale in (B) is enlarged >10-fold relative to (A). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The second major component detected, ethanol, is a commonly used solvent. The polyimide resin is solid at room temperature, and thus degassing under vacuum is not an efficient method to remove solvent remaining from resin synthesis. Nevertheless, large amounts of ethanol are generated during imidization, and this requires mitigation. From TGA experiments, >20% by weight of solvent evolves during the initial imidization ramp and hold. The large weight loss from solvent volatilization poses challenges, particularly when producing thicker, multi-ply polyimide laminates, as volatiles can be trapped within the layers. This solvent volatilization (a) requires longer processing times to remove the volatiles, (b) raises the possibility of porosity if the solvent is not sufficiently removed, or (c) may potentially cause blistering when ramp rates and temperatures are excessive [24].

To illustrate how the analysis of volatiles can be deployed, we describe one approach to reducing the amount of ethanol released during cure of polyimide. In particular, by simply reducing the concentration of ethanol present, we can relax the processing restrictions, ultimately allowing for higher ramp rates, shorter dwells, and a shorter overall cycle time. Because the monomer is solid at room temperature and begins to crosslink upon heating, vacuum degassing is not an option. Instead, the monomer can be lyophilized (freeze-dried) to remove much of the ethanol, simply by addition of water and subsequent freeze-drying. Because water and ethanol are completely miscible in all amounts (whereas the polyimide is insoluble in water), the ethanol can be removed with the water during sublimation. This process also has the advantage of not affecting the out-life of the resin, as there is no heating step.

Fig. 9 shows that after only one lyophilization cycle, the amount of weight lost during cure drops by almost a factor of two, from 21.5% to 11.9%. The plot shows weight loss versus time, and the cure cycle is plotted on the same graph. The data indicates that freeze-drying can be used to remove

residual solvent and demonstrates how volatile analysis can be employed to address processing problems. Admittedly, the chemistry involved is likely to be complex, and there may be side reactions that generate ethanol during cure. Nevertheless, lyophilization can be an effective measure to mitigate volatile release. Note that without the data from the spectroscopic traces in Fig. 8, the reduction in cure-induced volatiles shown in Fig. 9 would not have been possible. Unambiguous identification of volatiles, coupled with understanding the kinetics of volatile release, were required to diagnose and remove the solvent remaining from monomer synthesis.
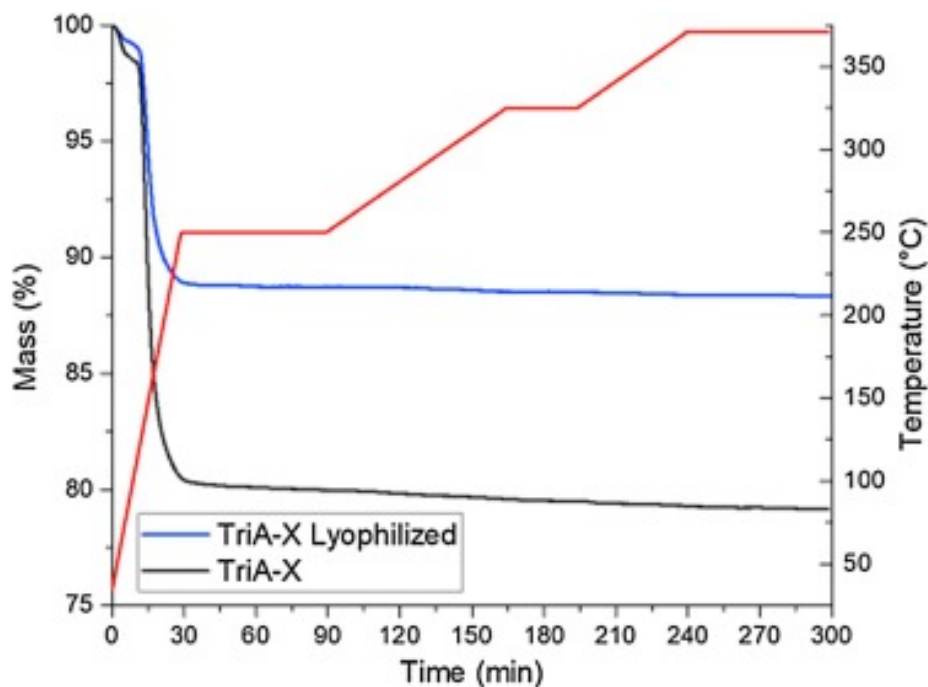

Fig. 9. Mass loss during cure for a polyimide sample cured before and after lyophilization. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.5. Resin system 5: polyimide prepreg

Fig. 10A below shows the FTIR spectra when one ply of polyimide prepreg is heated within the RC. Not surprisingly, the main volatile components released during the imidization dwell were

ethanol and acetaldehyde, although concentrations were lower than in the neat resin. Carbon dioxide

was also detected during the cure, although sulfur dioxide was not, supporting the hypothesis that

SO2 was a residual contaminant originating from the synthesis of the imide monomer. Fig. 10B

shows the first 60 min of the plot in Fig. 10A, the period during which most of the volatiles are
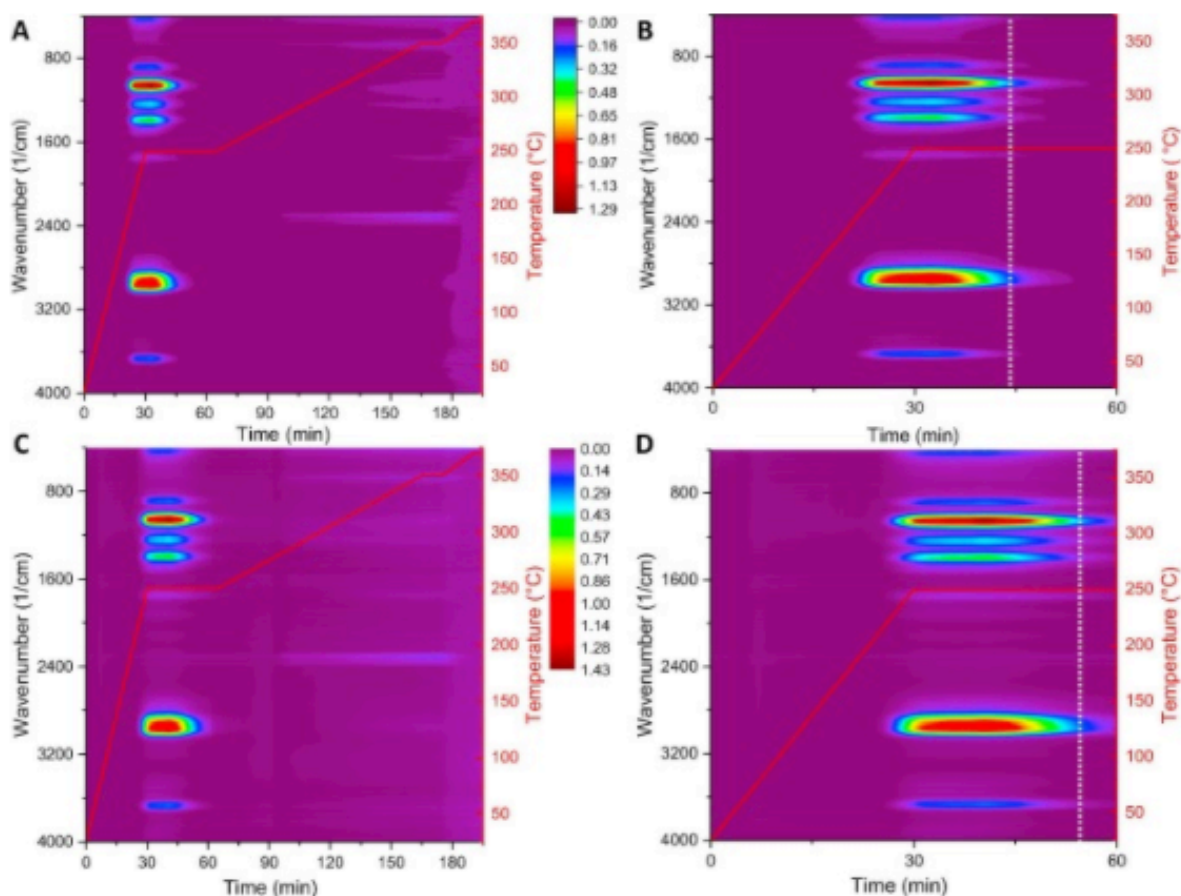
generated.

Fig. 10. (A) Spectroscopic traces for a 1-ply polyimide prepreg (B) Spectroscopic traces for the first 60 min of a 1-ply polyimide prepreg. Refer to (A) for intensity scale. (C) Spectroscopic trace for a 3-ply polyimide prepreg. (D) Spectroscopic trace for the first 60 min of a 3-ply polyimide prepreg. Refer to (C) for intensity scale. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 10C shows spectroscopic traces generated from three plies of polyimide prepreg cured

within the RC, and to facilitate comparisons to the one-ply sample, the first 60 min of this plot is

also enlarged and presented as Fig. 10D. Comparing Fig. 10B and D, it takes ~25% longer for the ethanol and acetaldehyde to clear from the cell during the imidization dwell, even when the sample sizes are similar. The white dotted lines on Fig. 10B and D show approximate times when the volatiles have cleared the cell. The data in Fig. 10 indicate that volatiles egress gradually from the prepreg stack due to diffusion limitations. These limitations are less apparent when analyzing only a single ply of prepreg. (The period of volatile release can depend on the ramp rate and/or the dwell temperature. In such cases, the RC/FTIR can be used to reveal that dependence and thus guide efforts to design cure cycles that limit volatile-induced defects.) Note that the imidization reaction here initiates abruptly, as evidenced by the sudden spike in spectroscopic intensity during the initial ramp. However, it takes much longer for volatiles to evacuate from the three-ply stack, and thus laminates require a long imidization dwell. As discussed previously, proper lyophilization of the polyimide resin before the resin is combined with the fibers in the prepreg can reduce the dwell time required, simply by reducing the amount of volatile to remove [24]. The data set indicates that the RC/FTIR approach can be useful in identifying manufacturing challenges for a particular resin, as well as pathways to process optimization.

4. CONCLUSIONS

We have demonstrated the utility of a temperature/pressure reaction cell coupled with an FTIR spectrometer for in situ quantification of cure-induced volatile release. Example studies were presented to illustrate the ability to quantify the kinetics of water release during cure in epoxy prepregs, the effect of pressure on a benzoxazine/epoxy resin blend, and to identify volatiles released from a polyimide resin powder and prepreg. The reaction cell was used to replicate the temperatures, times, and pressures relevant to the cure cycle of the composite. In all cases, we were able to identify

changes to process parameters or pre-treatments to either broaden the process window, decrease cycle time, or mitigate/minimize defects in the composite product.

The RC/FTIR method described here overcomes some of the major limitations of conventional characterization techniques, particularly TGA/FTIR or TGA/MS, when used for analysis of volatiles generated during composite processing. Using only these conventional methods, we would not have been able to quantify cure-induced volatile release and recommend process improvements, as the volatiles emitted from TGA samples were well below the detection limits of the FTIR, even with the most sensitive detectors. Only via the RC/FTIR approach were we able to generate sufficient amounts of volatiles for detection and quantification. Also, conventional characterization techniques typically do not allow users to simulate and assess the effects of applied pressure during processing, which, in the case of benzoxazine/epoxy composites, ultimately enabled us to identify a simple remedy to suppress volatile release during RTM.

While the work described here describes a general method for in situ quantification of volatiles and demonstrates the utility of the method, challenges remain. At present, the RC/FTIR setup cannot be used under vacuum, a condition frequently encountered in composite processing. However, this is a limitation that stems from the instrumentation available, rather than an issue inherent to the technique. Additionally, it is difficult to quantify the amounts of volatile being generated at a particular time (i.e., in grams), especially when multiple species are present. Despite these limitations, we have built a system capable of simulating open- and closed-mold environments, capable of reproducing pressures up to 450 kPa and temperatures up to 400 °C, while simultaneously identifying any cure-induced volatiles with greater sensitivity than traditional techniques such as TGA/FTIR.

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