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Path-dependent bond-line evolution in equilibrated core honeycomb sandwich structures

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ABSTRACT

During co-cure of honeycomb core sandwich panels, composite facesheets are cured and concurrently bonded to the core, introducing complex interactions that can lead to unsatisfactory bond-line formation. In this work, an *in situ* co-cure fixture is employed to directly observe the adhesive during processing and identify defect formation mechanisms specific to the bond-line. Relating fillet quality to imposed core pressure reveals the non-linear effect of core pressure. High pressures suppressed voids; intermediate pressures resulted in void growth and entrapment within deformed fillets; and low pressures led to void rupture and small, irregular fillets. Experimental results aided in developing a model to predict void growth in the bond-line. The findings presented here provide insight into the physics controlling the adhesive bond-line evolution during co-cure, which can inform manufacturing decisions to produce higher-quality honeycomb core sandwich structures.



KEYWORDS

Sandwich structures; honeycomb core; epoxy prepregs; thermoset adhesives; defect formation; cure behaviors; process monitoring; autoclave processing

1. Introduction

In this study, we clarify the physical mechanisms by which porosity forms in the adhesive bond-line during co-cure of honeycomb sandwich structures, and assess the dependence of these mechanisms on material and processing parameters. Additionally, we use the insights gained by these observations to develop a simplified predictive model for defect formation.

Co-cure of honeycomb sandwich panels reduces manufacturing time for sandwich structures by combining two processes – facesheet consolidation/cure and facesheet-core bonding – into a single step [1].

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However, coupling facesheet consolidation with adhesive bond-line formation introduces complex phenomena and material interactions (including multi-phase flow, dynamic pressure gradients, dissimilar cure kinetics, and intrinsic material variations) that are not well-understood. Developing an understanding of the physical mechanisms of defect formation and creating predictive tools for co-cure phenomena can inform processing decisions to increase manufacturing efficiency.

Prior research on the adhesive bond-line formation in sandwich structures has typically focused on producing parts with superior mechanical properties. Grimes [2] identified fillet size as the primary factor affecting bond-line performance in honeycomb core sandwich structures, with larger adhesive fillets providing greater shear, peel, and flatwise tensile (FWT) strength. These results were corroborated in studies that focused on determining the processing parameters that influence bond-line formation, with different studies concluding that cure temperature [3], compaction pressure and heating rate [4], and adhesive film thickness [5] strongly affect the bond-line. Resin viscosity [6] and solvent content [7, 8] were identified as important material parameters in bond-line formation.

Several studies have investigated the effect of applied pressure on adhesive bond-line behavior in various processing situations. Reducing the vacuum level (i.e. increasing the absolute pressure) was shown to reduce bond-line porosity when bonding flat panels under vacuum [9, 10]. For vacuum-bag-only (VBO) co-cure of sandwich structures, Nagarajan et al. [11] demonstrated that vacuum level, as well as moisture content and core type, can have inconsistent effects on fillet quality and mechanical performance (e.g. reducing the vacuum level increased peel strength for standard aluminum core but decreased peel strength for vented core). Alteneder et al. [12] employed a technique to impose super-ambient gas pressure within the core prior to cure, reducing facesheet porosity and core crush during autoclave cure.

For the VBO co-cure of sandwich structures, Tavares et al. used an apparatus consisting of a tool plate with a recessed pocket, enabling the measurement of core pressure during the cure of "half sandwich" structures to characterize facesheet permeability [13, 14]. Varying initial core pressures were imposed using different perforation patterns in the adhesive and prepreg to vary permeability [15], with intermediate average core pressures during processing yielding greater G_{IC} values. Kratz and Hubert [16–18] used a similar apparatus to characterize facesheet permeability and develop a predictive model for core pressure during co-cure. Observations specific to the adhesive primarily echoed two previous results: (1) large, void-free fillets were stronger than small or porous fillets (characterized by peel strength [16]), and (2) at room temperature, the adhesive film tended to act as a barrier to gas transport [18].

A common limitation in the works cited above is the reliance on post-processing analysis of parts to optimize manufacturing methods, a practice which is resource-intensive and material-specific. Further, by considering only the final state of the bond-line, the studies highlighted provide limited insight into the underlying, time-dependent mechanisms by which bond-lines form. To address these concerns, predictive, physics-based models requiring minimal material characterization have been developed.

Rion et al. [19] developed a model for fillet height based on surface energy minimizations, with contact angles for the adhesive-facesheet and adhesive-core interfaces as the primary inputs. The model, however, is limited to secondary bonding, so prepreg resin bleed into the core can be ignored, and void-free fillets are assumed. Similarly, Chen et al. [20] developed a predictive model for the fillet size in sandwich structures produced with a selfadhesive prepreg, with prepreg permeability and compaction as inputs (the characterization of which is detailed in a prior publication by the same group [21]). However, the same assumptions as the Rion model still apply: there is no interaction between prepreg and adhesive resin (here, because no separate adhesive is used), and voids are not considered. These assumptions restrict the utility of the models for the general co-cure case.

Likewise, void growth models are available, but assumptions limit the relevance to sandwich structures. Kardos et al. [22] developed a diffusion-based model for the growth of a water vapor void in a CFRP laminate, with others updating the model to improve accuracy [23–25]. Préau and Hubert [26] adapted this diffusion-based model for an adhesive film used in repair. However, factors such as geometric complexity and presence of two resins complicate similar modeling for co-cure of sandwich panels.

We elucidate complex dynamic interactions between the physical phenomena during co-cure by employing an *in situ* visualization tool [27]. This fixture affords direct observation of the bond-line in a "half-sandwich" structure under conditions identical to processing, providing visual data and insights that can be related to processing time and temperature, as well as autoclave, bag, and core pressures. Parts were fabricated using an "equilibrated core" configuration (e.g. when one facesheet is perforated [28, 29]), in which core pressure could be controlled explicitly through a direct path to the vacuum bag. Thus, observed time-dependent behavior could be linked to

Table 1. Testing parameters for samples manufactured in the in situ co-cure fixture. All pressures are absolute.

Test	Turne	Core/Bag	Autoclave	Compaction
Test	туре	Pressure [KPa]	Pressure [KPa]	Pressure [KPa]
1	Aluminum Bonding	0	101.3	101.3
2	Aluminum Bonding	50.7	101.3	50.7
3	Aluminum Bonding	101.3	239.2	137.9
4	Co-Cure	0	101.3	101.3
5	Co-Cure	25.3	101.3	76
6	Co-Cure	50.7	101.3	50.7
7	Co-Cure	76	101.3	25.3
8	Co-Cure	101.3	239.2	137.9
9	Co-Cure	152	239.2	87.2
10	Co-Cure	202.6	239.2	36.6
11	Co-Cure	253.3	377.1	123.8

specific pressures (as opposed to an initial or average value for an evolving core pressure, which has typically been used in prior literature [12, 15]). Results indicated a non-monotonic relationship between void content and pressure, dependent on the adhesive viscosity during void growth for a given pressure.

Mass loss as a function of both temperature and pressure was characterized for both the adhesive and prepreg resin used in the study, and results informed *in situ* observations. Notably, an increase in the rate of mass loss in the prepreg resin correlated well with observed void formation. When considered together, *in situ* videos, polished cross-sections, and mass loss data provided a consistent description of behavior for this material set during co-cure.

Finally, we used experimental results to guide model development to describe defect formation in honeycomb sandwich panels. Both in situ visualization and mass loss data provided necessary material parameters for a simplified model that could predict the onset temperature of void growth (i.e. the model predicts when void growth begins, but does not describe time-dependent evolution of void size) for a range of core pressures. The model was used to design two staged pressure cycles, one predicted to suppress void growth and one to facilitate void growth. Experimental validation of these cycles demonstrated the path-dependence of defect formation mechanisms identified in this work. These results are a necessary first step towards further analysis of the co-cure process through experimentation and model development.

2. Experimental

2.1. Materials

The adhesive selected for this study was a modified epoxy (Henkel Loctite EA 9658 AERO) supplied as a film supported by a non-woven glass fiber (NWG), with an areal weight of 320 g/m^2 . Models for the cure kinetics and viscosity were previously reported [30]. The manufacturer-recommended cure cycle consists of a 60 min cure at $177 \,^{\circ}$ C, with a ramp of $2.2-4 \,^{\circ}$ C/min.

The prepreg used for facesheets in co-cured samples consisted of a plain-weave carbon fiber fabric

impregnated with a toughened epoxy designed for structural aerospace applications (Hexcel Hexply 8552S), intended for autoclave cure. Several variants of the 8552 resin exist, including the "S" version used in this work, which is manufactured using a solvent-based method to achieve full impregnation. The standard resin (8552) has been characterized previously, and published models for thermal properties, including cure kinetics and viscosity, are available [31, 32]. The models in this study were adapted from Hubert et al. [31] based on supplied 8552-1 resin film (non-solvated), which closely approximates the kinetic and rheological behavior of 8552S prepreg. A separate study on the solvated prepreg has confirmed the presence of residual solvent (methyl ethyl ketone [MEK]) using Fourier-transform infrared spectroscopy [33], which was not expected to significantly affect the cure rate at the amount identified (<2% by mass).

The core used was a phenolic-coated Nomex honeycomb (Gill Corporation HD132), with 3.2 mm (1/8 in) hexagonal cells, 12.7 mm (1/2 in) thickness, and a density of 48 kg/m^3 (3 pcf). These materials are typical of those used for autoclave cure of honeycomb sandwich panels.

2.2. Sample fabrication and in situ visualization

To monitor the formation of the bond-line during processing, "half sandwich" panels were fabricated in an *in situ* co-cure fixture that allowed for observation of the bond-line during cure. The fixture is described in detail elsewhere [27], and consists of an aluminum base with a recessed pocket into which the honeycomb core is placed. The bottom of the core pocket includes a glass window, and glass spacers can be inserted into the pocket to accommodate various core thicknesses while enabling visualization of the bond-line.

An aluminum lid can be bolted onto the base, and the enclosed cavity can be pressurized to simulate autoclave conditions. Both the lid and the base feature integrated heating elements with separate controls. Autoclave, vacuum bag, and core pressures (through ports in the core pocket) were imposed



Figure 1. Fillet measurement method for Test 1 (top) and Test 8 (bottom). The bounding box is set where the adhesive contact angles with both the cell wall and facesheet reach $\sim 0^{\circ}$. Dimpling, which results from bending of the facesheet, is defined as the difference between the bottom of the box at the cell wall and the adhesive film thickness measured at the outer bound of the fillet.

and measured with separate pressure sensors. Temperature was measured and recorded using four thermocouples within the fixture.

Samples generally consisted of a honeycomb core (76 mm \times 76 mm) and a facesheet and adhesive film (both 102 mm \times 127 mm). For samples with aluminum facesheets, the aluminum was abraded with 60-grit sandpaper and cleaned with acetone. Co-cure samples were assembled with four plies of prepreg ([0°/90°]_{2s}). Before layup, a release agent was applied to the surface of the fixture base and recessed pocket. The core was placed into the pocket, and the adhesive and facesheet were placed overtop, leaving an edge-band over the tool surface. Two layers of sealant tape were placed around the

edges of the facesheet to restrict air transport to the through-thickness direction, simulating the center of a large part. A perforated release film, layer of breather, and vacuum bag were overlaid on the prepreg facesheets. This layup configuration simulated the bag-side facesheet of a typical autoclave-cured sandwich structure.

The cure cycle for all tests consisted of a 60 min dwell at 110 °C and a 120 min dwell at 177 °C, with a 2°C/min heating rate, per the manufacturer-recommended cycle for the 8552S prepreg. No room-temperature vacuum hold was included prior to heating. Prescribed vacuum bag, core, and autoclave pressures were imposed before the temperature cycle was started, and these pressures were held constant throughout cure. Because the core cavity was equilibrated with the vacuum bag, core pressure was controlled rather than evolving during cure. In every test, the vacuum bag and core pressures were equilibrated to eliminate gas transport through the facesheet and adhesive, and to limit void content to initiallyentrapped air and evolved gases. Dynamically-changing features (such as facesheet consolidation), however, could not be controlled.

For this study, samples were fabricated for 11 different material and core pressure conditions, as listed in Table 1. Pressures are given in absolute units, and the compaction pressure is defined as the difference between the autoclave and bag pressures. In this study, we focused on the effect of core pressure (i.e. the gas pressure to which the adhesive was exposed) on development of the adhesive bond-line. The tests were divided into three categories depending on the material and processing parameters: (1) bonding to an aluminum facesheet; (2) co-cure with sub-ambient or ambient pressure in the vacuum bag and core; and (3) co-cure with super-ambient pressure in the vacuum bag and core.

Aluminum-bonded samples were fabricated at full vacuum (<5 kPa), half vacuum (50.7 kPa), and ambient (101.3 kPa) core pressures. Because an impermeable aluminum facesheet was used, a vacuum bag was not necessary to eliminate gas transport through the facesheet. However, for the vacuum and half-vacuum tests, a bag was used to provide compaction pressure to ensure intimate contact between the adhesive film and the core. Autoclave pressure was set to 101.3 kPa (i.e. vented to ambient pressure) for simplicity. For the ambient pressure test, there was no compaction pressure applied as a result of bag pressure, so autoclave pressure was set to 239.2 kPa (20 psig, typical of autoclave pressures during co-cure) to ensure contact between the adhesive and the core.

The sub-ambient co-cure tests included five pressure levels, ranging from full vacuum to ambient pressure at increments of \sim 25.3 kPa (0.25 atm). One



Figure 2. Time-lapse video frames for aluminum bonding under vacuum (Test 1) and at ambient pressure (Test 3). t_1 is the initial state, t_2 is halfway through the first temperature ramp, and t_3 is the end of the first temperature ramp.

sample was fabricated for each testing condition. To assess reproducibility, two additional samples were produced for select conditions: aluminum bonding at 0 and 101.3 kPa and co-cure at 0, 101.3, and 253.3 kPa. Core pressure was the focus of this study, and previous literature has shown it to be a dominant parameter for porosity formation in the adhesive. Therefore, differences in compaction pressure were neglected and autoclave pressure was set to 101.3 kPa (i.e. vented to ambient) for simplicity. However, to avoid a zero-compaction case arising from ambient pressure throughout (bag, core, and autoclave), an autoclave pressure of 239.2 kPa (20 psig) was used when the bag and core were set to ambient pressure.

For the super-ambient co-cure tests, pressure in the bag and core was supplied using nitrogen gas. Tests were conducted at 152, 202.6, and 253.3 kPa (1.5, 2, and 2.5 atm). To prevent the bag from detaching from the tool surface, autoclave pressure was maintained at a level greater than the bag and core pressure, and so a pressure of 239.2 or 377.1 kPa (20 or 40 psig) was applied before pressurizing the bag and core to the specified levels. Otherwise, procedures for these tests were identical to those for the sub-ambient tests.

2.3. Microstructural analysis

Samples fabricated in the *in situ* co-cure fixture were also analyzed following cure to quantitatively

assess the bond-line quality. Two sections (50 mm \times 25 mm) were cut from each sample – perpendicular to the ribbon direction and at the center of the cells – and polished using a grinder-polisher (Buehler MetaServ). Measured fillet size may change dependent on the location within the cell, and a constant plane was chosen so that fillets could be compared directly. The polished sections were then imaged using a video microscope (Keyence VHX-5000) to inspect the bond-line microstructure. Each section contained \sim 20 fillets, and thus \sim 40 fillets were evaluated for each test.

Image processing software (Adobe Photoshop) was used to assess the fillet quality, as diagramed in Figure 1. Fillets were bound by a square with opposite corners set at where the adhesive reached a 0° contact angle with the cell wall and the facesheet (or, if the contact angle does not reach 0° , where the adhesive thickness reaches 0). This approximation was selected for its combination of robustness, repeatability, and ease of use in the software. Fillet height was the height of the square plus an adjustment for dimpling, which was defined as the difference between the bottom edge of the square and the adhesive thickness at the inside corner (Figure 1B). This definition of height was chosen for consistency with previous literature (e.g. [5, 15]). Dimpling was used solely as an adjustment factor for consistent measurement of fillet height and was not itself

analyzed in this study. For aluminum-bonded samples, dimpling was 0. Void area was measured within the area bounded by the top and inside edges of the square, the cell wall, and the facesheet. Therefore, voids contained within the adhesive layer not factored into the height were still counted.

2.4. Resin outgassing

Outgassing of the adhesive (a factor contributing to porosity) was analyzed by mass loss using thermogravimetric analysis (TGA, TA Instruments Q5000 IR). Tests were performed at ambient and vacuum pressures with a heat cycle consisting of a 2° C/min ramp to 350 °C. The heating rate was selected to be consistent with the cure cycle used to fabricate half-sandwich samples. The prepreg was also tested to assess whether residual solvent could be a factor in defect formation observed in the *in situ* time-lapse videos. Sample size was ~5 mg.

3. Results and discussion

3.1. Sample fabrication and in situ visualization

Figure 2 shows frames from time-lapse videos (videos for all tests are provided as supplemental material) for bonding with an aluminum facesheet, recorded at times t_1 , t_2 , and t_3 (temperature and viscosity for these times are shown in Figure 3). Under vacuum, voids formed in the adhesive (Test 1, t_2). However, these voids burst or collapsed prior to gelation of the adhesive, redistributing the adhesive onto the cells walls and resulting in small but void-free fillets (Test 1, t_3). At ambient pressure, the adhesive displayed negligible void growth, and bond-line formation was dominated by viscous flow (Test 3, t_2).

The half-vacuum test behaved similarly to the ambient case: some minor bubbling of the adhesive was observed, but not enough to redistribute the resin through bursting of bubbles. In all cases, nearly all activity occurred during the first ramp in the temperature cycle, and the bond-line was largely stagnant during the first dwell and through the remainder of the cure.

For co-cure tests, frames from time-lapse videos were recorded at times t_1 , t_2 , t_3 , and t_4 , as shown in Figure 3. During the first temperature ramp, co-cure samples behaved like the aluminum facesheet counterparts. Under vacuum, the adhesive foamed and redistributed onto the cell walls (Test 4, t_2 and t_3). At ambient core pressure, fillets were observed to form by adhesive flow (Test 8, t_2). Some clear prepreg resin, differentiated from the grey adhesive, flowed into the fillets from the facesheet.

Behavior of the co-cure samples diverged from that of the bonded samples beginning with the

second temperature ramp. In the sample under vacuum, after the initial bubbling of the adhesive during the first ramp, further void growth was negligible (Test 4, t_4). However, at ambient pressure, voids grew during the second ramp (Test 8, t_4) and remained trapped in the bond-line after cure.

Time-lapse videos were compared to modeled cure kinetics and viscosities for the adhesive and prepreg resins, indicating that void growth observed during the second ramp in the ambient-pressure case occurred as the prepreg resin reached its minimum viscosity and the adhesive viscosity began to increase. Increasing temperature and decreasing prepreg resin viscosity facilitated volatilization or growth and transport of entrapped voids, and these voids inflated the adhesive that remained in the final bond-line.

Tests at partial vacuum levels demonstrated an approximately linear effect of pressure on defect behavior, with observed void growth decreasing as core pressure was increased. At ambient core pressure, voids grew in the bond-line as the viscosity of the adhesive increased. However, as pressure was decreased, some bubbles burst prior to gelation. Under full vacuum, nearly every void ruptured before the adhesive gelled, resulting in a bond-line with negligible apparent porosity. Two potential explanations exist for this: (1) from Henry's law, for a given temperature, gas solubility in a liquid is proportional to its partial pressure in the atmosphere the liquid is exposed to, so lower pressures could cause evolution of dissolved volatiles in the adhesive or prepreg resin prior to the gelation of the adhesive, and (2) decreasing the core pressure increases the difference between the void gas and the core pressures, increasing the rate of void growth and thus the likelihood that bubbles can grow and burst prior to adhesive gelation.

The sub-ambient tests described above demonstrated the effectiveness of vacuum in reducing void content in the bond-line through the evacuation of entrapped air, volatiles, and other potential void sources. In contrast, increasing the bag and core pressures beyond ambient level was expected to decrease void content by suppressing evolution of dissolved gases in solution and providing sufficient resin pressure to overcome gas pressure within voids to restrict growth.

An applied pressure of 253.3 kPa suppressed most porosity during the second temperature ramp, although voids were not entirely eliminated (Test 11, t_2 , Figure 3). Some voids grew during the first temperature ramp, attributed to air entrapped between prepreg plies during layup or at the prepreg/adhesive interface that could not be evacuated due to the absence of applied vacuum. However,



Figure 3. Time-lapse video frames for co-cure tests, with temperature profile and modeled viscosities of both the prepreg and the adhesive. Times are denoted on the temperature plot.

during the second temperature ramp (t_4) , only minimal void growth was observed, which had little effect on the shape of the bond-line. At 151.9 and 202.6 kPa core pressures, void growth during the second temperature ramp was reduced but not fully suppressed.

3.2. Microstructural analysis

Data for the fillet heights and void areas is presented in Figure 4, and selected micrographs are shown in Figure 5. For bonding to aluminum, void area was relatively low (\sim 3–50% of corresponding co-cure values) for all pressures. At ambient core



Figure 4. Height (top) and void area (bottom) versus core pressure for aluminum bonding and co-cure.

pressure, no significant void growth was observed. Under vacuum, voids formed but collapsed or burst before the adhesive gelled, providing a nearly voidfree final bond-line. The half-vacuum tests had roughly double the void content than the other bonding samples, but the values were still low compared to co-cured samples. Average height was \sim 25% greater at ambient core pressure, as the bursting of voids and redistributing of adhesive at lower pressures reduced fillet height (e.g. in Figure 5A, adhesive can be seen on the cell wall above where the adhesive contact angle with the wall reaches 0°). At all core pressures, fillet height was low $(\sim 50-70\%)$ compared to the respective co-cure test (in which resin from the prepreg could bleed into the bond-line and increase fillet size).

For co-cure tests, results fell into three regions of quality (determined based on cited literature, e.g. [2, 3, 6], with quality increasing as height increases and void area decreases) (Figure 4). Region 1 consisted of tests at 0 and 25.3 kPa core pressures. Porosity was relatively low, as voids that grew tended to burst or collapse before the adhesive gelled. However, collapsing voids also led to reduced fillet height. In Region 2 (core pressures of 50.7, 76.0, and 101.3 kPa), adhesive bubbles did not grow (and thus did not burst), and so fillet height was roughly twice that of Region 1 tests. However, during the second ramp, volatiles from the prepreg were trapped in the adhesive, resulting in large and numerous voids. Thus, void areas for Region 2 tests were roughly five to ten times larger than for Region 1 tests.

Region 3 (super-ambient tests) produced fillets that were both tall and void-free. Like in Region 2, core pressure during the first temperature ramp was sufficiently high to prevent the growth and collapse of bubbles that resulted in reduced height in Region 1. Further, the core pressure was sufficient to suppress volatilization of the prepreg during the second temperature ramp, reducing void content relative to Region 2. These three regions demonstrate the nonmonotonic behavior of bond-line quality, a phenomenon that has led to inconsistencies in reports of quality versus core pressure in prior literature.

Variability between fillets in individual tests was large, with relative standard deviation ranging from $\sim 10\%$ to 60% for height and $\sim 100\%$ to 375% for void area. Despite the large variability, results were reproducible. Qualitatively, *in situ* videos for repeated tests at each condition demonstrated similar behavior. Additionally, for height and void area, deviation from fillet to fillet within each sample was greater than the deviation between different samples.

3.3. Resin outgassing

Results for the TGA tests are presented in Figure 6. Due to high noise levels in the data for the adhesive under vacuum, this data set has been smoothed (using a moving average *via* the "smoothdata" function in MathWorks MATLAB 2017) for cleaner visualization. Mass loss in the adhesive was low, \sim 0.4% at ambient pressure and \sim 1.0% under vacuum at 177 °C. The rate of mass loss was relatively constant within the processing window, although a slight increase was observed around 150 °C when under vacuum.

Up to ~ 110 °C, the prepreg behaved like the adhesive: mass loss was low ($\sim 0.5\%$ at 110 °C and ambient pressure) and increased slightly under vacuum ($\sim 0.8\%$ at 110 °C), while the rate of mass loss remained constant. As temperature increased



Figure 5. Micrographs for: (a) Test 1 (aluminum bonding, vacuum), (b) Test 3 (aluminum bonding, ambient), (c) Test 4 (cocure, vacuum), (d) Test 8 (co-cure, ambient), (e) Test 11 (co-cure, super-ambient).

beyond 110 °C, however, the rate of mass loss increased, peaking at ~160 °C. Under vacuum, this increase began at ~ 110 °C, while at ambient pressure, the increase did not begin until 125 °C. Additionally, the degree to which this accelerated mass loss occurred was greater under vacuum: mass loss in this temperature range was $\sim 1.5\%$ under 0.5% vacuum and at ambient pressure. Decomposition, marked by a second increase in the rate of mass loss beyond the processing window, was estimated to begin \sim 225 °C.

The temperature range (110 °C to 225 °C) corresponds to the first dwell and second temperature ramp (110-177 °C) of the cure cycle used to fabricate samples in the co-cure fixture, and the TGA data was consistent with observations from the in situ videos and fillet data obtained from micrographs. Voids trapped in the final bond-line tended to grow during the second temperature ramp, which corresponds to increased mass loss in the prepreg. For the sub-ambient tests, porosity increased as core pressure increased. Additionally, this temperature range matched temperatures at which MEK was identified in FTIR spectra of vapors from the prepreg [33], indicating that the increased mass loss and void formation observed was due to volatilization of residual solvent in the prepreg.

The TGA data confirmed that lower pressures resulted in greater mass loss and an earlier onset of

the increased mass loss rate. At the dwell temperature ($110 \,^{\circ}$ C), volatiles were able to evolve and evacuate under vacuum, but not at ambient pressure. In the corresponding *in situ* videos, bubble growth and bursting was observed throughout the dwell when under vacuum. The extent of bubbling decreased as pressure increased until, at ambient pressure, void growth did not begin until the second temperature ramp, when the adhesive viscosity also began to increase. The increased capacity of the prepreg to evolve and evacuate volatiles under vacuum, especially during the first temperature dwell, resulted in lower volatile content available to evolve while the adhesive viscosity was increasing, thus reducing porosity in the bond-line.

4. Void growth modeling

4.1. Model development

The model employed was adapted from one published by Préau and Hubert [26] for diffusion-based void growth in an adhesive used for repair applications. The representative element consists of a single, spherical void surrounded by an infinite pool of resin, such that (1) there are no interactions between bubbles, (2) the bubble size is small relative to the bulk resin volume and does not affect the shape of the entire structure, and (3) the



Figure 6. TGA results for 9658 NWG adhesive (top) and 8552S prepreg (bottom). Data for the adhesive under vacuum has been smoothed.

concentration of volatile in the bulk resin is constant and uniform. The radius r of the void is given by

$$\frac{\partial r}{\partial t} = \frac{D}{r} \beta \left(1 + \frac{r}{\sqrt{\pi Dt}} \right) \tag{1}$$

where D is a diffusion term and β is a "driving force" related to the volatile concentration gradient:

$$\beta = \frac{c_{bulk} - c_{vs}}{\rho_g} \tag{2}$$

where c_{bulk} is the volatile concentration in the resin, c_{vs} is the volatile concentration at the void surface, and ρ_{g} is the density of the gas in the void.

By considering only when void growth begins, and not the size of the void, predictions using Equation (1) can be simplified to avoid the prior assumptions (specifically of individual and small voids) that are not representative of the void growth observed in time-lapse videos. The onset of void growth occurs when $\frac{\partial r}{\partial t}$ changes from negative or zero to positive, which is determined solely by β . All other terms in Equation (1) are always positive. The condition for void growth, therefore, is

$$\beta = 0 \quad \Rightarrow c_{bulk} = c_{vs} \tag{3}$$

The bulk resin concentration is assumed to be constant. For moisture-based voids, this concentration has been represented as a function of the relative humidity ϕ in which the material is conditioned [26]:

$$c_{bulk} = \frac{k\rho_r \phi^2}{100} \tag{4}$$

where k is a proportionality constant representing solubility of the volatile in the resin, and ρ_r is the resin density. Because the solvent was in the prepreg resin, material properties including resin density were considered for the prepreg resin, and voids that grew in the prepreg due to the solvent were assumed to transfer to the adhesive.

Similarly, concentration at the void surface is a function of the instantaneous partial pressure of the volatile(s) in the void, which varies with temperature and applied pressure:

$$c_{\nu s} = \frac{k\rho_r}{100} \left(100\frac{P_\nu}{P_\nu}\right)^2 \tag{5}$$

 P_{ν} and P_{ν}^{*} are, respectively, the partial pressure and the saturated vapor pressure of the volatile in the void. If the void is assumed to be pure solvent, the adhesive is assumed to transfer all pressure to the void, and surface tension effects can be ignored, P_{ν} equals P_{core} . Temperature dependence of the saturated vapor pressure is given by the Clausius-Clapeyron equation, so Equation (5) can be written as

$$c_{vs} = 100k\rho_r P_{core}^2 \left(P_{ref}^* exp\left[-\frac{\Delta H_{vap}}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right] \right)^{-2}$$
(6)

 P_{ref}^* is the vapor pressure of the volatile species at reference temperature T_{ref} (e.g. the standard boiling point), ΔH_{vap} is the latent heat of vaporization, and R is the universal gas constant.

For water as a volatile, as in ref. [26], k can be characterized through humidity conditioning resin samples, which is restrictive for non-water volatiles. Alternatively, by treating c_{bulk} as a material constant independent of conditioning, Equations (3) and (6) can be combined and solved to give k:

$$k = \frac{c_{bulk}}{100\rho_r} \left(\frac{P_{ref}^* exp\left[\frac{-\Delta H}{R} \left(\frac{1}{T_{onset}} - \frac{1}{T_{ref}}\right)\right]}{P_{core}} \right)^2$$
(7)

where T_{onset} is the temperature at which void growth begins. Using Equation (7), k can be computed if c_{bulk} , the volatile species, and the onset temperature for a single core pressure are known. The



Figure 7. Comparison of individual bubble (left) and "foaming" behavior (right). Individual bubble growth was not considered when determining the onset of void growth.

onset temperature of void growth can then be predicted for any given cure cycle.

4.2. Determination of model parameters

Computing solubility parameter k using Equation (7) first requires characterization of the volatile species causing the voids, the concentration of volatile in the resin, and the temperature at which void growth begins for a given core pressure. The volatile species for the prepreg used in the study has been identified as MEK [33], and the latent heat of vaporization ΔH_{vap} and standard boiling point T_{ref} (where P_{ref}^* is atmospheric pressure) have been previously reported [34].

Volatile concentration in the resin was estimated using TGA data presented in Section 3. As discussed previously, two regions of mass loss were identified: first, up to ~110°C, mass loss attributed to moisture occurred, followed by an increased rate of mass loss due to volatilization of MEK. The concentration of MEK in the resin was determined as the percent mass loss under vacuum in this temperature range (110 °C to decomposition at 225 °C), which was 1.5%. Multiplying by the density of the resin yielded the volatile concentration in the desired dimensions of mass per unit volume. This definition requires two simplifications: (1) all the residual MEK was able to be evacuated within the temperature range while under vacuum and (2) stages of mass loss do not overlap (i.e. mass loss in this temperature region was solely due to volatilization of MEK).

In situ time-lapse videos presented in Section 3 were used to determine the onset temperature of void growth for a given core pressure. As different void behaviors were identified, growth of individual bubbles (attributed to moisture or initially-



Figure 8. Experimental and model results for critical temperature as a function of pressure.

entrapped air) was ignored, and void growth was defined to begin when foaming behavior attributed to the solvent was observed (Figure 7). Because temperature could not be measured directly in the bond-line, the temperature reported here was the average of those measured on the outside of the bag and of the tool plate. For the initial calculation of k, Test 8 (co-cure at ambient core pressure) was selected, and void growth was observed beginning at 117.3 °C (temperatures recorded outside the bag and at the tool plate were, respectively, 118.1 and 116.5 °C).

4.3. Results and discussion

Using the parameters determined above, a value of 1.26×10^{-3} (dimensionless) was computed for k, which is within roughly one order of magnitude of the value reported for water in an epoxy adhesive [26]. Note that, for small changes in temperature, k does not vary significantly (e.g. the ± 0.8 °C range measured corresponds to a change in k of less than



Figure 9. Two sample pressure cycles demonstrating path dependence of void growth. In Cycle A, core pressure is maintained at a level greater than the critical pressure, thus no void growth is expected. In Cycle B, the delayed increase in pressure causes the critical pressure to increase beyond the core pressure, and void growth is predicted during this period.

 \pm 5%). This value of k was then used to predict void growth onset temperatures for the remainder of the co-cure tests presented in Section 3, with results presented in Figure 8. No experimentallyobserved temperature could be identified for the two extreme cases. For the full vacuum test, a core pressure of 1 kPa was used in the model to ensure a solution, and the predicted onset temperature was below room temperature. In the in situ video, void growth occurred immediately as the viscosity decreased (i.e. resin viscosity and not temperature was the limiting factor), and so no reliable onset temperature could be determined. At 253.3 kPa core pressure, the onset temperature predicted occurred while the adhesive was gelling, and no foaming was observed. For the remaining tests, the model showed agreement with experimental data.

4.4. Pressure cycle design and validation

The model can be used to design pressure cycles to mitigate void growth for a given temperature cycle. With k known, Equation (7) can be rewritten to give P_{crit} as a function of temperature:

$$P_{crit} = \frac{P_{ref}^*}{10} \sqrt{\frac{c_{bulk}}{k\rho_r}} exp\left[-\frac{\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]$$
(8)

 P_{crit} is the minimum core pressure necessary to suppress void growth at the respective temperature, and any pressure below this level may cause void growth. For a given temperature cycle, P_{crit} can be computed using material parameters for the prepreg (which contains the residual solvent), and any void growth in the adhesive due to evolution of the solvent is assumed to stop when the adhesive gels.

Figure 9 shows this critical pressure during the temperature cycle used to fabricate samples in Section 3, along with two sample pressure cycles demonstrating the path-dependence of void growth. Each cycle consists of two identical pressure levels (101.3 kPa and 253.3 kPa), with the timing of the pressure increase offset by \sim 40 min. While the model predicts a critical pressure of 407.9 kPa at the maximum processing temperature of 177 °C, this prediction does not consider adhesive or prepreg resin viscosity. Recall that in Section 3, a core pressure of 253.3 kPa sufficed to suppress void growth prior to gelation of the adhesive. Here, in Cycle A, the core pressure is increased prior to the second temperature ramp so that the core pressure always exceeds the critical pressure. In contrast, for Cycle B, the pressure increase is delayed to the middle of the temperature ramp, thus critical pressure increases beyond the core pressure. Consequently, void growth is expected during this portion of the cure cycle.

To validate the model predictions, parts were produced using both staged Cycles A and B, following the procedures for samples fabricated in the in situ co-cure fixture detailed in Section 2. During the initial stage of ambient (101.3 kPa) pressure in the bag and core, an autoclave pressure of 239.2 kPa was applied (as in Test 8). To maintain constant compaction pressure, autoclave pressure was increased to 391.2 kPa prior to raising the bag and core pressure to 253.3 kPa. In Cycle A, the second stage began prior to the second temperature ramp, while in Cycle B, this stage began during the temperature ramp ($\sim 150 \,^{\circ}$ C).

In situ observations for Cycle A were comparable to those of Test 11 (with 253.3 kPa core pressure). During the first temperature ramp and intermediate dwell, critical pressure remained below the 101.3 kPa core pressure, and void growth was suppressed. Initially, in the second stage of the pressure cycle, core pressure was greater than the critical pressure. As temperature increased during the second ramp, the critical pressure surpassed the core pressure, but the adhesive viscosity had also increased. Some void growth was observed in regions where the prepreg resin (which gels after the adhesive) was exposed through openings in the adhesive.

By delaying the pressurization to the middle of the second temperature ramp, Cycle B yielded behavior similar to Test 8 (with 101.3 kPa core pressure). Critical pressure surpassed core pressure while adhesive viscosity was low (\sim 100 Pa·s), and void growth occurred. The increase in pressure briefly resulted in a core pressure greater than the critical pressure, collapsing some of the voids and resulting in reduced porosity compared to Test 8.

Void area data reflected trends observed in in situ videos. Cycle A was within an order of magnitude of Test 11 $(0.0032 \text{ mm}^2 \text{ and } 0.0076 \text{ mm}^2)$, respectively). Average void area for Cycle B (0.0520 mm²) increased nearly sevenfold compared to Test 11, as voids grew. However, because some voids collapsed when the core pressure was raised, this void area was a quarter that of Test 8 (0.2118 mm²). Overall, these results are consistent with predictions and demonstrate the utility of the model in determining whether void growth will quantitative predictions occur, despite not being available.

5. Conclusions

The time-dependent formation of voids in the adhesive bond-line during co-cure of honeycomb sandwich structures was investigated using an in situ cocure fixture, and bond-line quality was correlated to gas pressure in the core during processing. Notably, the greatest porosity levels occurred when process and material parameters led to entrapment of prepreg volatiles in the gelled bond-line, and pressurizing the core beyond ambient level suppressed volatile evolution and produced tall, non-porous fillets. Mass loss behavior was consistent with visual observations, with TGA measurements (along with FTIR spectra in a separate study) indicating a greater volatility of the prepreg compared to the adhesive due to residual solvent in the former. These results aided in the development of a simple void growth model to predict the presence of porosity for given processing conditions, and validation

tests using staged pressure cycles showed consistency with trends predicted by the model.

The results provide a physical description of bond-line formation during co-cure as well as insights into mechanisms responsible for the final morphology. In situ visualization was particularly valuable, affording understanding of the timedependent behavior of the adhesive bond-line that could be correlated to measured or controlled processing parameters. These observations clarified the path-dependence of defect formation, with certain behaviors linked not just to core pressure, but to timing within the processing cycle. For example, applying vacuum pressure in the core led to fillet disruption early during cure, which would result in short fillets in the final morphology regardless of the core pressure throughout the rest of processing. Likewise, validation studies demonstrated that void growth could be avoided as long as core pressure was always sufficient to suppress void growth, but increasing the core pressure after void growth began did not necessarily eliminate porosity in the final part.

This study also highlights the importance of material selection for honeycomb sandwich structures. For example, the primary defect source identified was the volatilization of residual solvent in the prepreg resin. While this prepreg may be suitable for monolithic parts, the inadequate transfer of pressure intrinsic to the discontinuous honeycomb core makes suppression of volatiles difficult, indicating that a solvent-free, hot-melt prepreg would be more appropriate. The difference in viscosity profiles specifically, the gel times - of the adhesive and prepreg resin was also shown to be a factor in void growth and so must be chosen appropriately. As the temperature at which the adhesive gels (and thus restricts further void growth) decreases, the pressure required to suppress volatilization of the prepreg solvent prior to adhesive gelation is also decreased. Therefore, the selection of an adhesive that cures at a temperature lower than the prepreg resin could be another strategy to produce defect-free parts.

The void growth model developed, while simplified, was able to guide processing decisions to suppress void growth. In a manufacturing setting, such a tool could aid in designing processing procedures that lead to defect-free parts and reduced material waste. The model we presented required reduced material characterization that was not restricted to water as the volatile species, facilitating the implementation of the model for different adhesives and prepreg resins. However, this model did not include any dependence on time, which restricts applicability only to determining *if* voids will grow. A prediction of the extent to which voids grow (e.g. in terms of bubble diameter or fraction of void area) requires a more robust model that includes time-dependent factors such as diffusion (Equation(1)).

We have focused on porosity formation specifically in the adhesive bond-line, but defects in the facesheet and core will also impact the overall performance of a sandwich structure. Furthermore, we only considered cases in which core pressure was controlled directly and equilibrated with the bag, conditions not representative of the general co-cure case in which core pressure evolves as a function of temperature and facesheet permeability. Insights gained here can be integrated with these other aspects to more fully describe the co-cure of honeycomb core sandwich structures and develop guidelines for robust and efficient manufacturing.

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Disclosure statement

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