Polymer film dewetting for fabrication of out-of-autoclave prepreg with high T through-thickness permeability

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Abstract: Polymer film dewetting on a substrate (independent of fiber bed architecture) was explored, developed, and demonstrated as a method to produce out-of-autoclave, vacuum bag-only (OoA/VBO) prepregs with high transverse permeability and process robustness. The dimensions of the surface openings created by dewetting were measured, and the percent surface area exposed was calculated. Prepregs were fabricated with continuous and dewetted (discontinuous) films to produce trial laminates. The laminates were cured under both standard and sub-optimal conditions, and were characterized before, during, and after cure. Laminates fabricated with dewetted resin consistently achieved near-zero porosity. In contrast, laminates with continuous film displayed high levels of porosity, particularly during sub-optimal cure. The findings demonstrate that dewetting can be used effectively to produce OoA prepregs with high through-thickness permeability, which can yield porosity-free laminates via VBO processing. Furthermore, these results elucidate aspects of resin dewetting that are critical in the creation of robust OoA prepregs.

Key words: prepreg, polymer-matrix composites, porosity, out of autoclave processing.
1. INTRODUCTION

Aerospace manufacturers seek to reduce costs of traditional composites manufacturing methods by producing autoclave-quality composite structures using out-of-autoclave/vacuum bag-only (OoA/VBO) methods [1,2]. The desire to shift away from autoclave cure is motivated by high acquisition and operation costs of autoclaves, resource-intensiveness, and throughput limitations, which can constitute a production bottleneck. Currently, VBO prepreg processing can match the part quality of autoclave cure, but only in optimal situations, while sub-optimal manufacturing conditions lead to greater defect levels, particularly porosity, and potentially degrade mechanical performance [3]. The major sources of porosity during prepreg cure are low process pressures (intrinsic to VBO cure) and incomplete evacuation of entrapped gases during processing.

VBO prepreg processing entails consolidating prepreg laminates within a standard industrial oven. Because the applied consolidation pressure is limited to 0.1 MPa (1 atm), the prepreg resin pressure can be insufficient to collapse bubbles that arise from entrapped air and/or evolved gases, which thus can remain in place during gelation and lead to porosity. The presence of entrapped gases in cured parts can lead to porosity levels as high as 3–5%, resulting in unacceptable mechanical properties and part rejection [4].

Technological advancements have been implemented to reduce porosity during VBO prepreg cure. Conventional VBO prepregs are pre-impregnated using a hot-melt approach, during which resin is formed into a thin film on backing paper (without the use of solvents) and pressed onto the fiber bed using rollers [4,5]. Hot-melt prepregging enables partial through-thickness impregnation of the fiber bed, which can be used to create dry, high-permeability gas evacuation pathways within the plane.
of the prepreg ply. These pathways allow rapid in-plane gas transport and, when combined with appropriate consumables (such as permeable edge-breathing dams), reduce void content within cured parts [6].

Despite these technological advancements, laminates produced by VBO prepreg processing cannot match the quality of autoclave processing in all manufacturing conditions [3]. Autoclave pressure effectively suppresses porosity caused by entrapped air, insufficient resin flow, and evolved gases, while VBO processing is inherently more susceptible to these problems. Process deficiencies (such as inadequate vacuum, insufficient air evacuation, and/or high humidity) generate voids in laminates fabricated with VBO prepregs. For example, VBO prepreg laminates are susceptible to micro-void formation if the material and thermal conditions shift the resin viscosity from the designed range [7]. These shifts can occur because of excessive out-time, which advances the initial degree of cure and increases moisture uptake, both of which alter the viscosity profile of the resin. Moisture absorbed from ambient humidity also will increase porosity in VBO-processed laminates, but not during autoclave cure [8]. Kardos developed a diffusion-based void growth model to explain this trend [9]. The gas pressure within the moisture-induced void can exceed the maximum resin pressure attainable with VBO cure at 120 °C. Such phenomena also can arise during autoclave processing, although autoclave pressures are typically sufficient to ensure adequate resin flow and to suppress moisture-based void formation.

Grunenfelder et al. showed that increasing air evacuation in the z-direction (transverse) virtually eliminated porosity caused by entrapped air or moisture in OoA/VBO manufacturing [10,11]. To increase the through-thickness permeability, the resin was distributed onto the fiber bed in
discontinuous strips, creating gaps that connect to the internal evacuation channels to form an interconnected, three-dimensional network. The prepreg (USCpreg [35]) was produced using a custom prepregging line to transfer the resin pattern onto the fabric using heated rollers. Using the USCpreg format, cured parts were produced with near-zero internal porosity and no surface defects even at non-ideal manufacturing conditions. The major limitation of the direct coating method was that the resin distribution depended entirely on the surface topology of the fabric, with resin transferring to the raised tow overlap sections but leaving recessed regions dry.

Tavares et al. [12] studied selectively impregnated prepregs called “semipregs” to assess the effectiveness of high-permeability prepregs for co-cure of honeycomb sandwich structures. Through-thickness air permeability was measured at room temperature and during the cure cycle for both a commercial semipreg (“Zpreg”) and an equivalent unidirectional prepreg (constructed with continuous resin). Results showed that the permeability of the semipreg was three orders of magnitude greater than the continuous film prepreg before and during the cure cycle, owing to a network of dry interconnected pore spaces. However, the large characteristic size of the dry areas within the semipreg necessitated use of a low-viscosity resin, resulting in unwanted resin bleed and high defect levels within the facesheets. Furthermore, the resin distribution within the semipreg consisted of linear strips, and the work did not describe a technique to create discontinuous patterns of arbitrary shape and size.

Roman reported a method to fabricate high through-thickness permeability prepreg [13]. In this method, resin was applied to the fiber bed using hot-melt coating. Next, the backing paper covering the resin layer was replaced with a polyester film. Covered with the film, the prepreg underwent a
heat cycle, during which the resin flowed away from fabric warps. As a result, openings were created in the film, allowing gas removal in the through-thickness direction. The resultant cured composite parts using this method exhibited near-zero internal porosity.

The methods of Roman rely on the phenomenon of fluid “dewetting,” the rupture of a thin liquid film on a solid substrate and the subsequent formation of islands or droplets. The reverse phenomenon is “wetting,” in which a liquid spreads and increases contact area with a solid surface. Wetting/dewetting is a result of intermolecular forces between the liquid film, solid surface, and the surrounding gas. The force balance between the adhesive and cohesive forces between these surfaces dictates the degree of wettability [14]. A useful parameter for gauging the wetting of a system is the spreading coefficient, S, which relates the interfacial tensions between a solid s, liquid l, and gas g denoted by γ_{ij} with i, j=s, l, g:

\[ S = \gamma_{sg} - (\gamma_{sl} - \gamma_{lg}) \]  \hspace{1cm} (1)

\[ S > 0, \text{ complete wetting occurs} \]  \hspace{1cm} (2)

\[ S < 0, \text{ partial wetting occurs} \]  \hspace{1cm} (3)

The surface energies are calculated from the Young Equation, a force balance along the solid-liquid interface [15]:

\[ \gamma_{lg} = \gamma_{li} + \gamma_{lg} \cos \theta \]  \hspace{1cm} (4)

Where \( \theta \) is the contact angle of the liquid droplet. However, polymer films may not dewet even if \( S < 0 \), because the film may be in a metastable state, i.e., below the glass transition temperature [16].

Kheghsi identified three stages of dewetting when forming new dry patches and the locations on which dry patches nucleate [17]. First, the liquid film must form on the solid substrate. Second, some disturbance must reduce the liquid film thickness to near zero. Approximate solutions to predict thickness prior to rupture were solved using the Navier-Stokes system augmented with conjoining force [17]. Finally, the liquid film ruptures and dry patches nucleate. As the dry patches grow, fluid material accumulates in a rim surrounding the growing hole. Dry patch formation will occur at a pre-existing patch or edge, or at a film-thinning disturbance caused by evaporation, drainage due to gravity (i.e., sharp/rough surface), and/or surface tension gradients.

The methods for producing prepregs with high through-thickness permeability described above are not suitable for unidirectional fiber beds, which are flat. The direct coating method described by Grunenfelder et al. requires the warps of twill fabric to pool resin. The second method (Roman) relies on the space created by overlapping tows as dewetting sites. Unidirectional (UD) fiber beds comprises the majority of the aerospace composites market. Therefore, a method is required to create high through-thickness permeability prepreg for all fiber bed architectures.

In this work, we describe a simple technique to create discontinuous resin patterns via polymer film dewetting on a substrate (versus being dependent on the fiber bed architecture). This technique can be used to create finely tuned patterns of various shapes and sizes. In addition, the patterned resin films created with this technique can be applied to any fiber bed, regardless of architecture. The technique can be used for lab-scale studies to explore and determine the limitations of prepregs with discontinuous resin patterns, and is potentially compatible with commercial processes used to produce prepregs. Here, we use the technique to produce UD prepreg with high through-thickness permeability.
permeability (UdSCpreg). In this process, resin film is first perforated on backing paper (the substrate) to create an array of nucleation sites, after which the film is heated to cause the film to recede from the nucleation sites. Finally, the dewetted resin is transferred onto UD tape by briefly pressing. In comparison to conventional OoA prepreg formats that feature continuous resin films, prepreg produced using this technique exhibited nearly void-free cured laminates, even under challenging cure conditions.

2. Materials

A UD carbon fiber bed (Fibre Glast Development Corporation, Ohio, USA) and a toughened epoxy resin (PMT-F4, Patz Materials & Technology, California, USA) were selected for the experiments. The epoxy resin was designed for vacuum bag curing and featured medium- to-dry tack. The fabric weight was 305 g per square meter (gsm) and the thickness was 0.36 mm. A binder of polyester fill threads stitched in one direction held the UD fibers in place. The tape exhibited negligible crimp, except around the binder. The resin was 76 gsm, yielding prepreg with a resin content of 33% by weight. The standard cure cycle included a ramp of 1.5 °C per min followed by a dwell at 121 °C for two hours. The resin storage life was two years at −10 °C, and the out-life was 120 days at room temperature.

Because of the resin thickness, the polymer dewetting process was not spontaneous when heated. To facilitate dewetting, nucleation sites were introduced using a hand-held spike roller (HR-2, Robert A. Main & Sons, Inc., New Jersey, USA). The spike roller pins were spaced at 6.35 mm, and the roller was passed over the entire film in straight passes. The dewetting process was carried out on silicone-coated release paper, which provided a low-energy surface [18] which was required for
dewetting. A standard oven (Blue M Oven, Thermal Product Solutions, Pennsylvania, USA) was used to heat the films for dewetting.

3. Film dewetting

3.1. Surface opening dimensions

The dewetting process was performed at three temperatures – 89 °C, 104 °C, and 119 °C – that were selected based on prior work and resin kinetics. For example, Roman created surface openings in a similar epoxy system at 104°C [13], midway between the temperatures of 119 °C (+15 °C) and 89 °C (−15 °C) chosen here. All three temperatures were below the specified curing temperature of the resin (121 °C), reducing the risk of changes in resin rheological properties due to dewetting.

The times used for dewetting spanned 15 s to 8 min, based on preliminary trials. This time range allowed for substantial variations of surface opening sizes at each sampling time, and allowed surface openings to reach maximum dimensions at each temperature.

The resin was thawed and cut to samples 75 × 150 mm on silicone-coated release paper. Nucleation sites were introduced into the films by spike rolling. The spike roller was passed over the entire surface without overlapping passes to achieve uniform spacing of nucleation sites. Subsequently, the sample was placed in an oven pre-heated to one of the specified nominal temperatures, and held for times of 15 s to 8 min. The sample was then removed from the oven and allowed to cool to room temperature.
Edwards et al. [19] reported the dewetting behavior of a dielectrophoresis-induced film as it formed into a single equilibrium droplet. Visual observations revealed that a rim formed, which receded at a constant speed and constant dynamic contact angle. This event was followed by relaxation into a spherical cap shape. The dewetting system presented here matches to the description of these two regimes. Fig. 1a and b show the dewetted resin on the substrate (silicone-coated backing paper) after 15 s and 4 min. At 15 s, a rim had developed with a width of about 0.3 mm. After 4 min, the rims of the adjacent holes had converged. The dewetted resin was then pressed onto UD carbon fiber tape using an unheated hydraulic press.

Each sample was examined using a microscope (VHX-5000, Keyence Corporation of America) over an area of 40 × 40 mm. Images of resin dewetted at 104 °C for 30 s and 2 min are shown in Fig. 1c and d. The images are representative of the surface opening sizes and shapes produced from the dewetting process. The images were converted to black pixels for fibers and white pixels for resin using image analysis software (ImageJ). The surface area exposed by dewetting was calculated from the numbers of black and white pixels:

\[ \text{Surface Area Exposed (\%) } = \frac{p_{\text{black}}}{p_{\text{white}} + p_{\text{black}}} \times 100\% \quad (5) \]

where \( p \) is the number of pixels. A greater percentage of exposed surface area indicates that a larger portion of the prepreg ply surface will consist of exposed dry fibers, rendering the prepreg far more permeable to gas than continuous resin films during consolidation.

The geometric features of the patterns were analyzed to quantify characteristics relevant to through-thickness permeability and impregnation. For example, Fig. 2a shows the percent surface area exposed...
exposed after 15 s to 8 min of dewetting at 89 °C, 104 °C, and 119 °C. At all three temperatures, the percent of surface area exposed sharply increased in the first 1–2 min, and then slowly increased with increasing time. The maximum exposure achieved across all three temperatures was 65% at 119 °C for 8 min. Fig. 2b shows the average diameter of the openings in each sample, where half this amount, or the radius, represents the distance resin must flow in-plane to fully wet the fiber bed. This flow length must be compatible with the resin cure kinetics, viscosity, and gel time to prevent incomplete saturation and flow-induced porosity. Second, the dimensions of the dry fiber regions will govern the prepreg impregnation time, with larger-diameter openings leading to longer times for air evacuation. Finally, opening size is also related to the likelihood of creating a continuous, interconnected, three-dimensional network of dry fibers within laminates formed of stacked prepreg plies. For example, openings larger than half the distance between the initial spiked nucleation sites (3.2 mm, in this case) are less likely to be sealed off during lay-up than openings with smaller dimensions.

The average diameter of the surface openings follows the same trend as the values of exposed surface area - the diameter increases sharply within the first 1–2 min, then slowly increases with time. The maximum diameter achieved across all three temperatures was 7.6 mm at 119 °C for 8 min. This distance is larger than the space between the initial nucleation sites created by the spike roller because many of the resin strands at the edges of the growing opening were breaking at this point. Edwards [19] developed a hydrodynamic model describing the rate of dewetting of a droplet. However, the model was developed for a different geometry (spherical cap) than the studies presented here (holes). Using the empirical data from this section (on surface opening sizes), the rate of dewetting, dR/dt, was measured to be 1.7 mm/min (or 2.9 × 10−5 m/s) at 104 °C during the first
regime. This rate can be used to calculate the Capillary Number, Ca, a description of the interaction between the resin and the substrate:

\[
Ca = \frac{\mu}{\gamma} \left| \frac{dR}{dt} \right|
\]

(6)

where \( \mu \) is the dynamic viscosity of the epoxy at 104 °C \( (6.088 \text{ Pa} \cdot \text{s}) \), \( \gamma \) is the interfacial tension of the epoxy and the substrate \( (\text{on the order of } 10^{-2} \text{ N/m})[20-22] \), and \( \frac{dR}{dt} \) is the rate of change of the radius of the surface openings \( (\text{on the order of } 10^{-5} \text{ m/s}) \). Here, the Capillary Number was determined to be on the order of \( 10^{-3} \), indicating that the dewetting process is dominated by the effects of surface tension rather than by viscous forces. Thus, surface tension forces will tend to minimize the surface area between the resin and the substrate.

The dewetted resin pattern can potentially affect the inter- connectivity and tortuosity of the dry pore network. Prepregs fabricated with continuous resin film do not feature breathe-out pathways in the through-thickness direction (Fig. 3a). However, the partial impregnation of the resin into the fibers allows for air evacuation at the edges of the prepreg. Applying a discontinuous resin pattern, on the other hand, creates additional pathways in the through-thickness direction for gases to evacuate. Due to random placement of plies during lay-up, smaller openings may not overlap with openings in adjacent plies (Fig. 3b). However, larger openings are more likely to overlap with another opening (Fig. 3c), resulting in an interconnected dry fiber network of pathways for gas egress. The formation of a highly connected network (i.e., breathing pathways to the surface) will promote rapid air removal.

Based on the results of dewetting experiments, dewetting conditions of 30 s and 2 min at 104 °C
were selected for subsequent tests. At 30 s of dewetting, the surface area exposed was 13%, and the average diameter of the openings was 1.7 mm. This condition represents a case in which full saturation of the fiber bed is likely, but openings may be sealed off during lay-up and/or prematurely during cure. After dewetting for 2 min, the exposed surface area was 50%, and the average diameter of the openings was 5.6 mm. This condition may result in incomplete wet-out of the fiber bed because of the large openings. However, a 3D network of interconnected dry areas is likely to form, facilitating air evacuation during the cure cycle.

Fig. 1. Top view images of resin dewetted at 104°C either still on the substrate (silicone-coated backing paper) or pressed onto unidirectional carbon fiber tape - (a) dewetted for 15 s on the substrate (b) dewetted for 4 min on the substrate (c) dewetted for 30 s pressed onto fiber bed (d) dewetted for 4 min pressed onto fiber bed. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 2. Dimensions of surface openings created by the dewetting process – (a) surface area exposed (b) average diameter of surface openings (where half this amount, or the radius, is the longest distance to wet-out during cure). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.2. Rheological Behaviour

Dewetting involves briefly heating resin film below the prescribed cure temperature, and this heat exposure introduces a risk of advancing the degree of cure. To assess the extent of partial curing, the viscosity profiles of three resin films – untreated, dewetted for 30 s at 104 °C, and 2 min at 104 °C
were measured over the recommended cure cycle using a rheometer (TA Instruments, Delaware, USA). A comparison of these three viscosity profiles against the cure cycle is presented in Fig. 4. All of the viscosity profiles decrease to a minimum after 57 min of the temperature ramp (1.5 °C/min to 121 °C), which are then followed by sharp increases in less than 8 min to over 104 Pa * s. The curves before and after dewetting show negligible differences.

The minimum viscosity and flow number values were obtained for the two dewetted resin samples and the untreated resin. These values were used to evaluate the effect of dewetting on rheological behavior. The flow number is defined as the integral sum of the inverse viscosity curve prior to gelation [23], and provides a measure of resin fluidity:

The minimum viscosity of the untreated resin was 5.6 Pa * s, while for both dewetted samples the value was slightly less − 5.3 Pa * s. The flow number for the untreated resin was 210.4 Pa−1, while the flow number for both dewetted samples was 212.4 Pa−1. These trends are counterintuitive because high-temperature exposure during dewetting should cause polymerization/cross-linking, which increases viscosity. However, the difference (0.3 Pa * s in viscosity, 2 Pa−1 in flow number) is negligible, and can be attributed to measurement variability.

Fig. 4. Viscosity profiles of resin without any dewetting treatment compared to resin dewetted for 30 s and 2 min at 104 °C. Times t₁, t₂, and t₃ correspond to the 1 h room temperature hold, the cure temperature ramp to 121 °C, and the 2 h cure dwell, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4. Prepreg fabrication and characterization

Two categories of prepreg with identical resin content (33wt%) were fabricated. “Control Prepreg” was produced by sandwiching UD carbon fiber tape between two 76 gsm continuous resin films, which replicated the architecture of conventional VBO prepps. Conversely, prepreg with discontinuous resin distribution was fabricated by com- bining UD tape with identically dewetted resin sheets. The resin in this category was dewetted at 104 °C for either 30 s or 2 min and, for the remainder of the paper, is designated as “Prepreg 104-30” and “Prepreg 104-120,” respectively. The
names designate the temperature and the time (in s) at which the resin film was dewetted. For both categories, resin was applied to the fiber bed by aligning and pressing constituents in an unheated hydraulic press (G30H-18-BCX, Wabash MPI).

4.1. Ammonia curing

Polished sections of uncured prepreg were prepared by exposure to ammonia vapor prior to polishing. Ammonia slowly cures epoxy resin at room temperature, fixing the resin in place with negligible flow [24]. This “ammonia curing” enables preparation of polished sections for evaluation of the structure of the prepreg stack before cure. The resin distribution in as-fabricated prepregs was examined to assess (1) the accumulation of resin due to the dewetting process and (2) the breathe-out pathways between layers for gas evacuation. Accumulated resin may lead to fiber bed deformation, primarily manifested as waviness due to the fibers conforming around the resin. Excessive waviness can lead to greater air entrapment and can also induce non-uniformity in laminate thickness, fiber volume fraction, or shape after cure, all of which adversely affect mechanical properties of the laminate.

To prepare samples for ammonia curing, resin and fiber tape pieces were cut to 75 × 75 mm squares. The resin - either a continuous film or a discontinuous pattern - was pressed on both sides of each fiber tape sample using a hydraulic press. Plies were then stacked symmetrically along the midplane in a [0/90]4s sequence, and each prepreg stack consisted of 16 plies. Next, the prepreg stacks were suspended for ten days above an ammonia bath inside a sealed glass vessel to slowly cure the epoxy [24].
Next, sections were cut from the ammonia-cured prepreg and polished for imaging. Images of polished sections are shown in Fig. 5. Fibers parallel to the surface [labeled “Fibers (0°)” in Fig. 5a] were unsupported and thus susceptible to tear-out during polishing, causing affected regions to appear black in the images. In addition, the fibers normal to the surface also tore out in places because of partial impregnation and insufficient support from the matrix. These areas appeared as dark regions within the fiber tows.

The prepreg fabrication protocols yielded distinctly different resin distributions. For example, the Control Prepreg exhibited evenly distributed resin ∼130 μm thick (Fig. 5a). Prepreg 104-30 showed a resin structure similar to that of the continuous film (Fig. 5b). The resin was evenly distributed with a thickness of ∼130 μm. In this case, there was also no clear evidence of accumulated resin due to the dewetting process. However, for Prepreg 104-120, resin accumulation was obvious (Fig. 5c). Some areas were resin-free, while others showed a resin thickness up to 280 μm. Resin accumulations in the prepreg may result in resin-rich regions in the cured laminate. Additionally, all three samples yielded minimal resin impregnation.

No fiber deformation was visible in laminates produced using Control Prepreg or Prepreg 104-30 (Fig. 5a and b). However, Prepreg 104-120 exhibited waviness in the fiber bed due to resin accumulation (Fig. 5c), where the average angle of fiber bed misalignment was 7.3° ± 2.3°. The average amplitude of the agglomerates was 0.22 ± 0.05 mm and the average wavelength was 2.45 ± 0.84 mm. This waviness can persist and propagate to cured parts, compromising mechanical properties.

4.2. X-ray Micro-CT

X-ray microtomography (micro-CT) yields 3D images and data that can be used to visualize prepreg microstructures, including entrapped gas bubbles and air evacuation pathways [25]. The ammonia-cured Control Prepreg and Prepreg 104-120 were imaged by micro-CT. The samples were cut using a diamond saw into 25 × 50 mm rectangles. Scans were performed using an industrial CT system (GE Phoenix Na-notom M) with voxel size 14 μm, source voltage 70 kV, source current 180mA, and exposure 500ms. The resulting series of parallel tomographic slices was used to visualize microstructural features and perform quantitative measurements.

The 2D and 3D images generated are presented in Fig. 6. The darker regions (black) represent void space, while the lighter regions (white-gray) represent solid space (fibers and resin). The 2D images at left show orthogonal cross-sections, with fiducial markers indicating the relative position of each slice. The upper 3D image at right is a selected sub-volume comprising 2-3 plies (of the 16 total plies), while the lower 3D image is a view of the in-plane direction of the fibers of all 16 plies.

Both the Control Prepreg and Prepreg 104-120 exhibit rod-like void spaces parallel to the fiber direction (e.g., areas enclosed in blue boxes). The Control Prepreg also exhibits large irregular void spaces (e.g., red boxes), consistent with prior observations of air entrapped between resin-rich ply interfaces [26]. Conversely, inter-ply air entrapment was negligible in Prepreg 104-120. The percent volumetric void space of the Control Prepreg and Prepreg 104-120 was 11.6% and 13.1%, respectively. The differences in void content and morphology are attributable to the discontinuous resin distribution in Prepreg 104-20 achieved by dewetting. This prepreg features less exposed resin surface area, reduces the likelihood of resin-on-resin mating, decreases risk of bubble entrapment, and increases the effective size of the dry pore network within multi-ply laminates. Altogether, the

CT data underscores the differences in internal microstructure between prepregs fabricated with continuous film versus discontinuous films.

4.3. Permeability Anisotropy

The effective (slip-corrected) transverse permeability was measured and compared for the Control Prepreg, Prepreg 104-30, Prepreg 104-120, and dry fibers. The transverse permeability of the experimental prepregs is expected to differ markedly from conventional VBO pre-pregs. A custom test fixture was used for the experiments [27], following the falling pressure method described by Tavares [28]. Plies of dry fabric or prepreg were laid over a cavity of known dimensions supported by stacks of honeycomb core. Measurements were recorded for 1-, 2-, and 4-ply laminates.
edges of the plies were sealed with vacuum tape to prevent edge-breathing and allow air evacuation only in the through-thickness direction. The laminates were covered with perforated release film and breather cloth, and vacuum-bagged. Vacuum was drawn in the bag to compact the laminate and create a pressure difference between the core cavity and the bag. The evolution of pressure in the cavity was monitored over time using a pressure transducer and data acquisition software (LabVIEW, National Instruments), and the measurements were used to estimate an effective permeability coefficient. All tests were performed at room temperature.

To obtain an average effective permeability value, two samples (replicates) were tested for each experimental configuration, with a minimum of five pressure decay trials per sample. Each trial was continued to the time at which the cavity pressure stabilized (indicating flow had ceased), and the configuration was then re-pressurized to begin the next trial. The data from the first trial was omitted because air evacuates more quickly when the consumables and plies have not been previously compressed.

Utilizing Darcy’s Law, the one-dimensional laminar flow of compressible air at isothermal and adiabatic conditions through a porous medium [27] can be described by

$$\frac{KAP_{Bag}}{L \mu V_{Core}} t = \ln \left[ \frac{(P_{Core}(0) + P_{Bag})(P_{Core}(t) - P_{Bag})}{(P_{Core}(0) - P_{Bag})(P_{Core}(t) + P_{Bag})} \right]$$  \hspace{1cm} (8)

where $K$ is the permeability scalar in the flow direction in m$^2$, $A$ is the cross-sectional area ($1.46 \times 10^{-2}$ m$^2$), $P_{Bag}$ is the pressure at the bag side ($5 \times 10^3$ Pa), $P_{Core}$ is the pressure at the honeycomb core side in Pa, $L$ is the lateral dimension in m, $\mu$ is the viscosity of air at room temperature ($1.85 \times 10^{-5}$ Pa * s), $t$ is time in s, and $V_{Core}$ is the volume of the core ($7.87 \times 10^{-4}$ m$^3$). Here, the vacuum
level is assumed to be 95% (corresponding to an absolute vacuum bag pressure of 5kPa). Plotting the left-hand side versus time yields a straight-line plot, the slope of which can be used to determine the effective air permeability of the prepreg, $K$.

A summary of the permeability values of the 1, 2, and 4 ply laminates versus fiber surface area exposed is presented in Fig. 7. The Control Prepreg is represented by 0% surface exposure, while dry fibers represent 100% surface exposure. The percent surface area exposed was 13% and 50% for Prepreg 104-30 and Prepreg 104-120, respectively.

![Figure 7. Through-thickness permeability values for 1, 2, 4, and 8 plies of prepreg. The value of 0% surface area exposed represents dry fabric, 100% represents continuous film, and the values in between represent the two levels of dewetting focused on in this work. Error bars were omitted for viewing clarity (statistical information can be found in Table 1). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image)

The transverse permeability of the experimental prepregs is expected to differ markedly from conventional VBO prepregs, and experiments were undertaken to measure this property. Resin
film dewetting substantially increases the room-temperature permeability of each laminate configuration.

For the Control Prepreg, little airflow was detectable for all ply counts, resulting in permeability values less than $0.1 \times 10^{-16}$ m$^2$. Kratz [27] reported similar results, and lack of air flow was attributed to the inherent topographical features of the UD tape (i.e., absence of gaps in the resin film). Prepreg 104-30 yielded four- to six-fold increases in transverse permeability (to values of $0.5–0.7 \times 10^{-16}$ m$^2$) as compared to the Control Prepreg. Prepreg 104-120 demonstrated a further increase in transverse permeability, with values 36–52 times greater than the values obtained for the Control Prepreg ($3.7–5.3 \times 10^{-16}$ m$^2$, and 30–50% of those of UD dry fibers. Tavares et al. [12] likewise reported that the air permeability of two plies of the semipreg format was three orders of magnitude greater than two plies of an equivalent continuous film format. The transverse permeability decreased slightly as ply count increased, owing to an increase in the tortuosity of the dry pore network, or possibly to differences in compaction and dimpling between thin (compliant) and thick (stiff) laminates (similar to Grunenfelder et al. [10]). However, single-ply and 8-ply laminates exhibited similar trends with respect to surface area exposed. As shown by Grunenfelder et al. [10,11], prepreg with greater transverse permeability generally results in more rapid air evacuation, and nearly eliminates porosity in cured laminates.
Table 1
Statistical data (average, maximum, and minimum) for the permeability tests run for the Control Prepreg, Prepreg 104-30, Prepreg 104-120, and dry fibers at 1, 2, 4, and 8 plies.

<table>
<thead>
<tr>
<th>Type</th>
<th>Ply Count</th>
<th>Sample Avg K (m²)</th>
<th>Sample Min (m²)</th>
<th>Sample Max (m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control Prepreg</td>
<td>1</td>
<td>8.4 x 10⁻¹⁸</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>2</td>
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5. Laminate characterization

5.1. In-situ visualization

Insights into air removal mechanisms during VBO cure of prepregs can be provided by use of a transparent tool plate, as described by Hu et al. In their work, they described a technique for in situ visualization of prepreg during cure [29,30]. Using similar methods here, 8-ply prepreg stacks were fabricated using Prepreg 104-30 and Prepreg 104-120. The stacks were laid against a glass window of an oven and vacuum-bagged with standard consumables, including edge-breathing dams. The standard cure cycle was used, and prepregs were observed during cure using a digital microscope (Dino-Lite US, Dunwell Tech, Torrance, CA).

Fig. 8 shows the progression of resin flow at the tool/part interface at different times during the cure cycle. Images in the first column show the surface openings during the room temperature vacuum hold. The second column shows the same openings during the heating ramp. At this point, the resin began to flow, primarily along the fiber direction. The third column shows surface openings during the cure dwell, at which point the openings were fully saturated with resin. However, vestigial evidence of the surface openings remains, manifesting as regions with a different visual appearance. These regions are fully saturated, but the resin film covering the fiber bed is marginally thinner than in adjacent areas. This indicates that aspects of the laminate microstructure were affected by the initial prepreg format (e.g., resulting in a different resin film thickness at the surface, or changes in fiber arrangement).
The sequences in Fig. 8 show that in-plane resin flow occurs primarily along the fiber direction due to the anisotropic in-plane permeability of the aligned fiber bed. Therefore, the radius of the openings represents the longest flow distance of the resin to complete saturation of the fiber bed. For this fiber bed, resin system, and cure cycle, full saturation of the visible area required 16 min more for Prepreg 104-120, which fully saturated after 41 min after the onset of the temperature ramp, than for Prepreg 104-30, which fully saturated after 25 min.

The images in Fig. 8 also show that in Prepreg 104-120, greater volumes of bubbles are trapped between the surface of the glass than in Prepreg 104-30. The greater volume of trapped air in Prepreg 104-120 can be attributed to the larger surface area of resin in direct contact with the glass. The tackiness of the resin combined with the natural surface texture invariably entraps air at the tool face, while dry fibers do not. The observation provides insight into how such prepregs will behave when laid onto tool molds. In particular, air entrapped at the surface between the tool mold and the prepreg can give rise to surface pits [31].

5.2. Surface defects and bulk porosity

Laminates were fabricated to assess levels of surface and internal porosity. Sixteen plies were stacked symmetrically along the midplane in a [0/90]4s sequence. Initially, each ply was cut to 150 × 150 mm, and after stacking, the edges of the stack were trimmed, resulting in dimensions of ∼140 × 140 mm. Two cure conditions were employed. The first condition consisted of a standard “ramp-hold” cure cycle, and standard vacuum bag consumables were used, including edge-breathing dams created from vacuum sealant tape wrapped in fiberglass and placed at the laminate perimeter. The second condition was identical to the first condition except for one key difference - the edge-
breathing dams were replaced with sealant tape to prevent in-plane air removal at the ply boundaries and allow air evacuation only in the through-thickness direction. This case was intended to approximate commonly encountered process conditions, which prevent or limit in-plane air evacuation in OoA prepregs, such as large or complex parts, parts with corners, etc.

Surface porosity and defects. Laminates produced with conventional VBO prepreg typically show surface porosity as a result of air entrapment at the tool face [31]. While surface porosity normally does not affect the mechanical performance of cured parts, it is a manufacturing defect that requires costly rework. Surface void contents were measured on the laminate surface facing the glass tool plate during the cure cycle. Images 38 × 38 mm were recorded using a digital microscope at 5 regions across the surface. Images were analyzed using software (ImageJ), and a series of manual steps to produce a binary porosity image. The surface porosity was calculated in the same manner as the calculation of exposed surface area described in Section 3.1. Finally, an average surface porosity was determined from the five images.

The surface porosity levels in laminates produced with and without edge-breathing were measured and compared, as shown in Fig. 9a. Edge-breathing yielded surface porosity near 1% when Control Prepregs were used, but the porosity levels dropped more than 50% when Prepregs 104-30 and 104-120 were used. When edge breathing during cure was eliminated, the difference was far more pronounced. Surface porosity was 8% in Control laminates, less than 1% in 104-30 laminates, and negligible in 104-120 laminates (Fig. 9a).

Laminates produced with Control Prepreg showed narrow surface pits 3–15 mm in length and 0.5–
2 mm in width (Fig. 9b). The distinctive elongated shape of the surface pits reflects the fact that air entrapped at the tool/part interface (and resin) flows primarily along the fiber direction. Laminates produced with Prepreg 104-30 were nearly free of surface porosity, showing occasional small pits (Fig. 9c). In contrast, laminates produced from Prepreg 104-120 showed a periodic array of equiaxed surface pits with spacing identical to the film perforations (Fig. 9d). Furthermore, the saturated film openings appeared as faint patches on the laminate surface, an effect attributed to fiber waviness and a thinner resin film in these regions. Such an artifact was not visible for laminates produced with Prepreg 104-30 (see Fig. 9c).

Bulk porosity. For measurements of bulk void content, mutually orthogonal sections were prepared from each laminate center. Cross-sections were polished to 4000 grit on a polishing wheel (LaboPol-2, Struers), and regions 20 × 5 mm were examined with a microscope. The average bulk void content of each laminate was measured in the same manner as the surface porosity.

For the Control Prepreg, the bulk void content nearly tripled, from 1.2% for standard cure conditions, to 3.2% with sealed edges (Fig. 10a). In contrast, for laminates created with Prepreg 104-30, the bulk void content was only 0.2–0.3% for both curing conditions, due to both fewer and smaller voids. For laminates created with Prepreg 104-120, the void content decreased further to 0.1% for both curing conditions. The insensitivity of dewetted prepgs to restricted in-plane air evacuation demonstrates that air evacuation occurred almost exclusively by breathe-out in the z-direction. Similarly, the results indicate that continuous film laminates, which represent equivalence to conventional VBO prepgs, rely exclusively on in-plane breathe-out pathways, which are far less robust and less effective than z-direction pathways, when present.

Martinez et al. [32] conducted studies on a thick laminate (64 plies) of unidirectional prepreg produced with dewetted resin films and compared the results to a control prepreg (128 plies of Cycom 5320-1, Solvay) of the same thickness. The control prepreg exhibited 8.5% internal porosity, while the laminate produced with discontinuous resin (with optimized distribution) showed 2.4% internal porosity. The study demonstrated that an increase in the flow distance in the through-thickness direction increases the amount of porosity in both the control prepreg and the prepreg produced with dewetted resin. However, the porosity value for the prepreg with dewetted resin is approximately 25% of the porosity of the control prepreg. These results indicate that the benefits of a discontinuous resin pattern, as described here, persist even as laminate thickness increases.

Two types of bulk porosity are observed when standard VBO pre-pregs are cured [33]. Inter-ply porosity consists of entrapped gas bubbles within resin-rich regions, typically between plies. Intra-tow porosity manifests within fiber tow bundles, and is generally attributed to incomplete resin infiltration due to inadequate resin rheological properties or process conditions. These pores are often classified as gas-induced and flow-induced, respectively. The Control Prepreg exhibited both inter-ply and intra-tow porosity (Fig. 10b), indicating both gas-induced and flow-induced porosity. The porosity type in laminates created with either Prepreg 104-30 or Prepreg 104-120 was primarily intra-tow porosity (Fig. 10c and d). These results indicate that the type of porosity produced using the discontinuous patterns was flow-induced and not from entrapped air.

Statistical Significance. The independent (unpaired) t-test is commonly used to determine if the means of two independent data sets differ significantly. A t-test was conducted for the data sets from

the Control Prepreg and either Prepreg 104-30 or Prepreg 104-120 for each cure condition (standard and sealed edges), and for both surface and bulk porosity. Due to limited sample sizes, each specimen was assumed to be an individual sample. The difference in the means of two sample sets is considered statistically significant if the p-value determined from the t-test is less than the chosen threshold value (usually 0.05) [34]. All tests were deemed statistically significant (p < 0.05) except for the surface porosity values of the Control Prepreg and Prepreg 104-120 under standard cure conditions, where the p-value was 0.071. Thus, the porosity values for prepreg produced with discontinuous resin patterns was significantly less than porosity values associated with the Control Prepreg.

5.3. Laminate structure

Earlier, in Section 4.1, uncured laminates created using Prepreg 104-120 were shown to exhibit resin-rich regions and fiber waviness, raising questions about the extent to which such non-uniformity would persist post-cure. The cross-sections used for internal porosity measurements provide the opportunity to assess the structure of the laminates, particularly with regard to this question of resin distribution and fiber integrity. The Control Prepreg exhibited a standard VBO prepreg microstructure, with resin evenly distributed within the fiber bed, uniform thickness between plies, and straight fibers (Fig. 10a). For both Prepreg 104-30 and 104-120, the laminates exhibited a similar structure post-cure, demonstrating that the consolidation process can achieve microstructural uniformity (Fig. 10b and c).

5.4. Bulk factor
The bulk factor is particularly important for curved parts, where a large bulk factor can result in wrinkling and/or bridging of plies. The bulk factor is the ratio of the initial thickness of the prepreg stack to the final thickness of the laminate:

\[ \text{Bulk Factor} = \frac{t_i}{t_f}, \quad t = \text{thickness} \tag{9} \]

In principle, the ideal bulk factor value is 1.0, a value that represents no change in thickness. However, prepregs that incorporate dry areas intrinsically possess bulk factors > 1.

Here, the bulk factor for the laminates created with Control Prepreg ranged from 1.17 to 1.26 depending on cure conditions (Fig. 11). As the extent of dewetting increased, the bulk factor increased to 1.30–1.40, representing increases of 5–13%. The increase in bulk factor is not unexpected, because the dewetting process accumulates resin locally, creating regions thicker (or thinner) than the original film thickness.

6. CONCLUSIONS

A method to create high through-thickness permeability VBO-OoA prepreg using UD carbon fiber tape was demonstrated and characterized. The approach was distinguished by the use of polymer film dewetting (prior to combining with fibers) to create periodic openings in the resin, through which gas evacuation during cure occurred during laminate consolidation. Laminates fabricated using prepregs produced by this method yielded near-zero void contents even when in-plane gas evacuation (edge breathing) was eliminated. In contrast, conventional OoA prepreg produced with continuous films resulted in laminates that exhibited much greater porosity (up to 8%) for both standard cure conditions and sealed edges.

The experiments revealed three important aspects for creating a prepreg format for high transverse gas permeability. First, a high level of interconnectedness of (dry) evacuation channels between plies must be achieved to create accessible pathways for gas evacuation and prevent premature occlusion. Measurements from permeability testing revealed that the transverse permeability increased as feature size dimensions of the discontinuous resin films increased. Therefore, the pathways are more accessible for through-thickness gas evacuation as feature sizes increase. Second, the openings must be sufficiently large to prevent closure of channels in laminates with large ply counts both during lay-up and/or during cure, but also small enough to prevent formation of surface defects and achieve full saturation during cure. The surface porosity results indicate that discontinuous patterns do exist that result in little to no porosity and without surface defects, although large feature sizes (large distances between resin features) will result in surface defects. Finally, the shape of the resin accumulations during dewetting can affect part quality by influencing the bulk factor, with greater dewetting levels potentially conflicting with lay-up and consolidation of contoured parts.

This work builds on previous studies [10,13], introducing a potentially scalable technique for producing OoA prepregs with discontinuous resin distributions from any fiber bed. Furthermore, the work demonstrated that in-plane discontinuity of resin (and not a specific prepreg embodiment) is the prepreg attribute that alone can nearly eliminate porosity in VBO-cured parts. Previous studies relied on a method for producing prepregs that relied on fabric topography to impart resin discontinuity. Furthermore, our work has not attempted to optimize the dewetting technique or resin
distribution, and thus further refinements and advances in efficiency may well be possible. The most effective distribution of resin for a given fiber bed and application is currently unexplored, but the dewetting technique presented here can be readily adjusted to produce a wide variety of complex patterns, a potentially fertile area for exploration.

OoA/VBO prepreg processing presently suffers from a lack of robustness in the manufacturing process, and unacceptable defect levels often observed in non-ideal manufacturing conditions or part geometries. The method described here [35] enables the production of UD fiber prepregs with discontinuous resin distributions, and such prepregs will enable manufacture of composite parts with low defect levels even in sub-optimal processing conditions. In addition, dewetting is potentially backwards-compatible with hot-melt prepregging, since in principle, imprint/de-wet steps can be incorporated into existing prepreg production lines. The inherent manufacturing robustness imparted by the methods presented can, in turn, expand the applicable uses of VBO prepregs within aerospace manufacturing and into other non-aerospace applications.

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References:


