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Eliminating volatile-induced surface porosity during resin transfer molding of a benzoxazine/epoxy blend

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ABSTRACT

We studied the mechanism of volatile-induced surface porosity formation during the resin transfer molding (RTM) of aerospace composites using a blended benzoxazine/epoxy resin, and identified reduction strategies based on material and processing parameters. First, the influence of viscosity and pressure on resin volatilization were determined. Then, *in situ* data was collected during molding using a lab-scale RTM system for different cure cycles and catalyst concentrations. Finally, the surface quality of molded samples was evaluated. The results show that surface porosity occurs when cure shrinkage causes a sufficient decrease in cavity pressure prior to resin vitrification. The combination of thermal gradients and rapid gelation can generate large spatial variations in viscosity, rendering the coldest regions of a mold susceptible to porosity formation. However, material and cure cycle modifications can alter the resin cure kinetics, making it possible to delay the pressure drop until higher viscosities are attained to minimize porosity formation.

1. Introduction

Resin transfer molding (RTM) has been used to produce composite structures for aerospace applications since the early 1980 s [1]. RTM is preferred for geometrically complex small to medium-sized parts that require low microstructural defect levels and excellent surface finish. The process can also be largely automated to improve production rates and repeatability, allowing medium to high volume production of high performance composites [2].

Resin transfer molding typically consists of three stages. The first, preforming, consists of preparing the fiber reinforcement by cutting and stacking plies of dry fibers, pre-shaping them by heated compaction, and placing them within the mold cavity. The second step involves injecting a pre-catalyzed but uncured thermoset resin into the heated mold cavity and saturating the fibrous preform. The final stage consists of imposing a temperature and pressure cycle that cures the resin while suppressing the formation of microstructural defects.

Voids are the most common type of defect encountered in RTM parts. They are often a result of air trapped within the mold cavity during injection, which can occur in the form of dry spots from converging flow fronts [3], or incomplete preform saturation due to an imbalance between the capillary and bulk flows that occur within dual-scale woven preforms [4,5]. Resin infiltration can be optimized by adjusting the gate locations [6] and inlet pressure [4] to minimize air entrapment. For a given injection scheme, air-induced voids can be further eliminated by applying vacuum to the mold cavity prior to (and during) injection, flushing additional resin through the system to evacuate bubbles, and increasing the applied hydrostatic pressure during cure [7]. During typical RTM, the microstructure achieved at the end of the injection stage remains largely stable during subsequent cure.

However, in some cases, voids can also arise from a second source: volatiles released by the resin at elevated temperatures. The positive hydrostatic pressure used during RTM (in contrast to vacuum-only resin infusion processes) was first developed to suppress the volatilization of water during the condensation cure of phenolic resins [1,8]. The source of volatiles is not limited to byproducts of polymerization – gas release can also occur due to residual solvents, vaporized monomers, dissolved air and moisture, degradation byproducts, or other impurities/contaminants. The detection, analysis, and control of volatile-induced porosity is particularly challenging because voids can form after injection, at any point during the cure stage.

1.1. Literature review

Voids in thermoset matrix composites are known to be detrimental to both mechanical properties [9] and cosmetic appearance

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[10]. However, while multiple studies have addressed the formation of voids during resin injection, relatively few studies have been devoted to the topic of void behavior during the curing stage of RTM.

The major void modeling approaches for thermoset composites derive from studies by Kardos et al. [11] and Wood and Bader [12]. Kardos et al. [11] developed a model for void nucleation and growth in the context of autoclave processing with an epoxy resin. They considered a diffusion-based mechanism, and assumed water to be the primary diffusible species. The model described both voids that exist initially at the onset of cure (and contain dry air or an air/water mixture), and voids that nucleate spontaneously at supersaturated conditions and contain only water vapor. They predicted a strong influence of initial dissolved moisture concentration on final void size and pressure. Furthermore, they noted that void growth cannot occur if the void gas pressure exceeds the saturated vapor pressure of the volatile species dissolved in the resin, and constructed a "stability map" showing the resin pressure required to suppress void growth as function of temperature and dissolved moisture content. Wood and Bader [12] described a similar diffusion-based model for void growth in autoclaved epoxy laminates, which instead considered nitrogen as the primary diffusible species. By experimentally determining surface tension, dissolved gas concentration, and the gas diffusion coefficient, they were able to predict time-dependent changes in bubble radii. Ledru et al. [13] developed a visco-mechanical void growth model (also in the context of epoxy-matrix composites cured by autoclave), which described a time-dependent void radius as a function of external pressure, temperature, viscosity, and surface tension, for voids containing a fixed amount of gas (i.e. omitting diffusion effects). They subsequently coupled the visco-mechanical model with a (water) diffusion-based model [14], aiming to improve upon previous diffusion-based models by accounting for viscosity and polymer crosslinking effects and by refining the predicted influence of hydrostatic pressure. They noted that, compared to diffusion-only models, visco-mechanical phenomena reduce void size. Like Kardos, they reported that initial dissolved volatile concentration and applied pressure were the most significant factors for void size, but they encountered difficulties in confirming the diffusion coefficient (which also strongly influences model predictions).

While the studies referenced in [11–14] consider autoclave processing, Lundström confirmed that, in resin transfer molding processes, hydrostatic pressure can cause gas dissolution and can collapse voids entirely [15]. The concentration of volatile species initially present in the resin also can be reduced prior to injection by vacuum-degassing [16], but the effectiveness of this technique is limited by the resin pot life, since degassing requires low viscosity and thus must be performed at high temperatures. Various time/temperature/vacuum pressure combinations can be used to influence the amount of volatiles extracted, but excessive vacuum-degassing increases the risk of pre-curing the resin, which can shorten the pot-life and complicate resin injection.

The volumetric change of thermoset resins during cure has been associated with defect formation. Eom et al. showed that, in three-dimensionally constrained thermoset resin, internal tensile stresses can develop due to chemical cure shrinkage, leading to void formation [17]. Furthermore, they found a critical stress criterion and developed process windows, providing guidelines to prevent void formation in autoclaved glass/epoxy laminates [18]. Similarly, Wisnom et al. [19] studied the effects of thermal and chemical volumetric changes on residual stresses in prepreg laminates, noting that it is possible for significant stresses to develop due to tool-part interactions before vitrification and even before gelation, where the resin may have a very low shear modulus but an appreciable bulk modulus. Merzlyakov et al. [20] also measured stresses in constrained thermoset resin during cure, finding that cure-induced tensile stresses were lower than expected, due to cohesive failure of the resin in the gelled (rubbery) state.

Cure shrinkage can be measured by monitoring sample thickness between parallel plates on a rheometer [21], using a pressure–volume–temperature (PVT) analyzer [22], by a gravimetric method [23], or by other methods [24]. The effects of resin volumetric changes on cavity pressure in RTM have been described by Kendall et al. [25], who noted pressure increases due to thermal expansion, as well as pressure drops attributed to cure shrinkage. Haider et al. [10] observed similar pressure drops due to cure shrinkage in automotive RTM panels, and correlated these with an increased surface roughness. Their unsaturated polyester resin exhibited much greater cure shrinkage (7–10%) than epoxies, which was successfully compensated by including a thermoplastic low profile additive (LPA). The expansion of LPA after gelation acted to reestablish positive mold pressure, resulting in high-gloss "class A" surface finishes. Boyard et al. [26] also noted increased surface roughness due to shrinkage-induced pressure drops in unsaturated polyester bulk molding compound (BMC), and used a dilatometer to develop a model for predicting cavity pressure. Recently, Landry and Hubert [27] described similar surface roughness due to shrinkage in thermoplastic short-fiber PEEK composites, developed a model to predict the pressure distribution, and correlated surface defects in colder zones with local pressure drops due to non-uniform shrinkage [28].

While the studies in the previous paragraph describe shrinkage-induced defects similar to those in our study, they differ in that none of the matrix materials exhibited significant volatility. For resins that can off-gas under deficient pressure, shrinkage-induced surface defects manifest as bubbles instead of increased roughness. This distinctive type of defect is particularly challenging to diagnose, since it can easily be mistaken for porosity due to air (trapped during injection) unless *in situ* observations are used to identify the nature of the porosity formation. Lab-scale RTM tools have been used previously to observe in-mold volatile release, for example by Pupin et al. [29]. Their "Nano RTM" contained a glass window, allowing *in situ* observations of volatile release in a phenolic resin. The primary volatile species was water – a byproduct of the phenolic condensation reaction – which was produced in such quantities that pressure alone could not suppress void nucleation. Void-free parts were obtained by removing the water via vacuum-degassing within the mold until gelation. The volatility of our resin, in contrast, is due primarily to residual solvent, which can be forced to remain dissolved in solution using only modest pressures. However, due to resin cure shrinkage, maintaining mold cavity pressure is not always possible. The combined effects of shrinkage-induced pressure drops and high resin volatility led to the topic of this work: volatile-induced surface porosity.

In this study, we consider the RTM processing of a blended thermoset resin consisting of benzoxazine and epoxy components. This combination is being investigated (by a commercial resin supplier) for structural aerospace applications due to expected improvements in high-temperature performance. Blending benzoxazine with epoxy has been shown to increase cross-link density compared to pure benzoxazine, increasing both the T_g and toughness [30,31]. This copolymer offers a compromise, in terms of both cost and maximum service temperature, between standard aerospace epoxies and ultra-high-temperature resins such as bismaleimides (BMIs) and polyimides. However, the complex polymer chemistry results in comparatively complex in-process behavior, particularly in terms of increased volatile release during cure. If not properly controlled, this volatility can result in significant surface porosity on molded parts (shown in Fig. 1), preventing the production of laminates with high quality surface finishes. During this study, sev-