VOLATILE-INDUCED VOIDS IN RTM PROCESSING FOR AEROSPACE

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Introduction

Resin transfer molding (RTM) may be used to manufacture void-free parts by means of several defect reduction strategies: optimized resin inlet locations that ensure complete preform wet-out, vacuum application within the mold cavity to remove entrapped air, and resin formulations that limit volatile off-gassing during cure. However, increased demand for composites with improved performance in severe environments has driven the development of innovative resin formulations [1] with complex chemical, physical and volatile release behavior during cure. The processing of such materials thus becomes much more challenging, and the relationships between resin properties, process parameters, and void formation must be re-evaluated. Here we describe a detailed study of volatile-induced void formation during the processing of a 177°C-cure heterocyclic modified phenolic-epoxy blended resin with potential applications in aerospace structures.

Resin characterization

First, the resin cure kinetics were studied using differential scanning calorimetry (DSC) to determine the evolution of the degree of cure for a variety of temperature cycles. Thermogravimetric analysis (TGA) was then used to quantify the mass loss behavior due to volatile release under atmospheric pressure for these cure cycles. Volatile release rates were found to be proportional to the rate of cure, showing an Arrhenius-type temperature dependence, but total weight loss was relatively insensitive to the cure cycle, ranging between 13-16% for all tests. The identities of the volatiles and their relative importance were measured with a coupled dielectric cure monitoring (DCM)/Fourier transform infrared spectrometer (FTIR) setup [2] capable of capturing information about the resin polymerization and the evolved gases from the same sample throughout cure. Lastly, a parallel plate torsional rheometer was used to measure viscosity prior to gelation, and cure shrinkage post-gelation by monitoring the gap between the parallel plates under constant normal force load control. A total post-gelation cure shrinkage of 9.5 – 10 % was measured at degrees of cure >95%.

Processing conditions & void formation

The relationship between resin behavior and void formation was investigated in manufacturing conditions using an instrumented lab-scale RTM mold with integrated heaters, pressure, temperature, and DCM transducers, and a rigid transparent mold wall allowing direct observation of void growth. First, a series of neat resin tests were used to determine the critical positive pressure required to suppress volatile-induced void formation. The threshold region of 135 to 170 kPa (all values absolute) was observed to prevent bubble nucleation over a cure temperature range of 160°C to 200°C. However, surface porosity was observed to persist even at the highest tested pressure, 790 kPa, for all studied cure

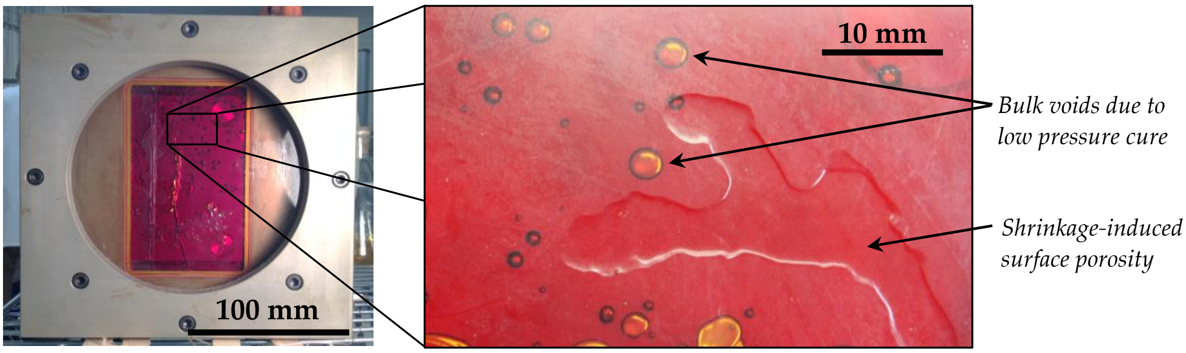

Figure 1: *Lab-scale RTM with neat resin sample cured at low pressure, containing both types of voids.*

temperatures, and for both neat resin and composite panels reinforced with a 5HS carbon fabric. This surface porosity appeared late in the cure cycle, and was accompanied by a sharp decrease in cavity pressure. The porosity was attributed to localized and uncontrollable pressure drops caused by cure shrinkage of the resin [3]. The distribution of the surface porosity was related to the temperature gradients in the mold, with larger defects near the coldest surface. This phenomenon can be explained by considering that, under a temperature gradient, a gelation boundary moves across the part, from the hottest location in the mold (and the first to gel) to the coldest location (and last to gel). The resin on the hotter side of the boundary, now solid, continues to shrink and exerts a tension on the colder, un-gelled resin. This tension counteracts the externally applied pressure and eventually causes the pressure at the colder, still-liquid tool-part surface to fall below the critical threshold value for suppressing volatiles, creating porosity in the finished part. In addition, the distribution of surface porosity is also influenced by the position of the inlet port. If left open and connected to the resin supply, uncured resin can reflow into nearby spaces made available by cure shrinkage, providing a smooth, void-free surface near the inlet. However, this phenomenon requires additional cure time for the newly-introduced resin, and its effective range is likely to depend on the preform permeability and the spatial configuration of the thermal gradients relative to the inlet(s).

Conclusions

Altogether, the study provides a broad, detailed understanding of the relationships between resin properties, process parameters, and the formation of volatile-induced voids in a next-generation blended RTM resin. The material performance benefits, namely a high T_g (202°C), the flame retardance of phenolics, and the superior strength and toughness of epoxies, are accompanied by a challenging combination of high cure shrinkage and volatile evolution. Most volatiles can be addressed by degassing prior to injection and by accurate thermal control, while the remainder can be held in solution with modest applied pressure. However, the more elusive problem of surface porosity induced by cure shrinkage and localized volatile-induced voids must still be addressed by strategies that reduce volatile release, limit thermal gradients or prevent pressure drops (e.g. flexible tooling).

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