VOLATILIZATION AND THE VACUUM INFUSION PROCESS

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If you have produced a part with vacuum infusion, at some point you've probably noticed what appear to be air bubbles in the finished composite.   Most likely, what you've seen isn't simply air from the surrounding atmosphere due to a leak in the bag: its vaporized resin! Understanding the relationship between resin selection, ambient temperature and vacuum pressure is critical to producing a properly cured part via vacuum infusion.

Recently, Polynova Composites participated in the evaluation of two polyester infusion resins. The test plans called for the production and testing of prototypical solid laminate test coupons wherein the resin system was the only variant. While the resin chemistries were thought to be similar, remarkably one system volatilized to the point of boiling at 24" HgV, whereas the other did so at 27" HgV at room temperature. Because boiling the resin would result in an unacceptable void content in the final part and vacuum pressure plays a critical role in the infusion process, Polynova Composites launched an investigation to better understand the factors involved.

Our goal was to improve understanding of the boiling behavior in the context of known characteristics of the resin systems. Thermodynamically, the boiling point of a liquid can be thought of as the disruption of equilibrium between thermal saturation and corresponding pressure saturation, where an increase in thermal energy or a decrease in pressure results in a phase change to the vapor state.

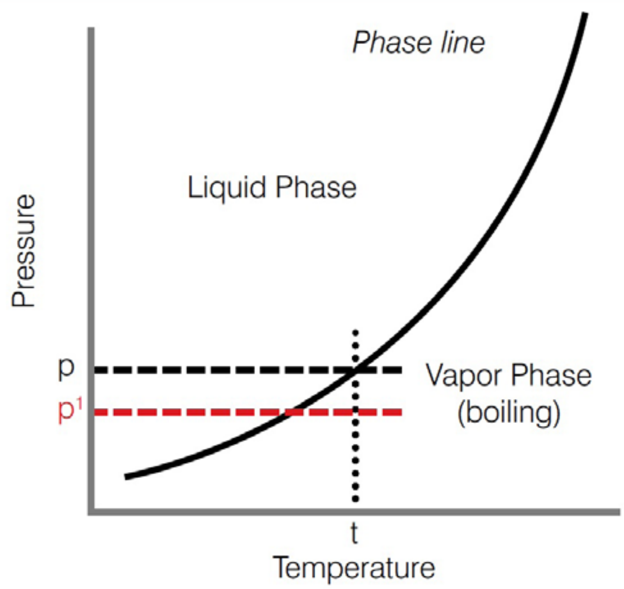

Figure 1. Hypothetical Phase Diagram

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We can visualize the phase change as a function of pressure and temperature with the aid of a phase diagram. Figure 1 is a portion of a hypothetical phase diagram, wherein the phase line separates the liquid and vapor phases. The phases are in equilibrium and co-exist with each other at any point on the line. Phase transitions occur at constant temperature and pressure at the points on this line. If the pressure is reduced at a given temperature (in this example from p to p1), the phase transition occurs and the liquid boils. Likewise, an increase in temperature for a given pressure would result in a similar phase transition.

If a single point along the phase line for a given liquid is known, such as the absolute boiling point (a.k.a. the boiling point temperature at atmospheric pressure), the curve can be reasonably extrapolated using thermodynamic equations.

Now let's turn to the resin system evaluation: plugging the potential bad actor compounds that might cause the resin to boil into the proper thermodynamic equations paints an interesting phase co-existence picture.

While we don't know the specifics of each resin's backbone, we believed both were based on isophthalic acid. In addition, both systems contain a fair amount of styrene (~35%). The resin systems differ in the type of initiator specified by the manufacturer, where one specifies methyl ethyl ketone peroxide (MEKP) as the free radical initiator, and the other specifies a 60/40 blend of cumene hydroperoxide (CHP) and MEKP as the free radical initiator. The system that volatilized at the higher pressure (-24" HgV) specified the MEKP, whereas the system with the lower volatilization pressure (-27" HgV) specified the CHP/MEKP blend.

The standard boiling point of styrene is 293°F MEKP's boiling point and decomposition point are 154.4°F. The standard boiling point of CHP may be derived from the literature boiling point of 213.8°F at 8 mm HgV as being ~503°F. Phase coexistence lines for each compound are plotted in Figure 2.

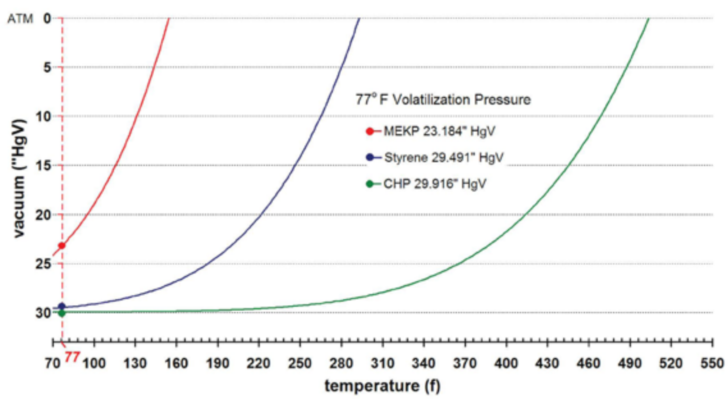

Figure 2. Phase Coexistence Line Plots for Styrene, MEKP and CHP

The boiling point pressures at 77°F are of particular interest, where MEKP boils at 23.184"; HgV and styrene and CHP boil at 29.451" HgV and 29.916" HgV, respectively. From the plots, one can reasonably conclude that the use of MEKP significantly influences the onset of boiling.

When we take a closer look at the pressures/ temperatures of interest for vacuum infusion processing, as shown in Figure 3, the effect becomes more apparent as the boiling pressure increases to 20" HgV at 95°F, a temperature that is well within the range of exothermic onset for many resin systems. This implies that while volatilization may not be visibly evident during the infusion, it will likely become prevalent just prior to resin gel.

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Just how much gas *could* be evolved? Reviewing the MSDS for the subject MEKP solution reveals that the actual weight percent methyl ethyl ketone peroxide in the solution is 34%. The rest of the solution is high boiling point components. If we assume a standard 1.5 weight percent addition of the MEKP solution to the resin, our actual MEKP content is 0.51 weight percent. For a 1,000-gram mass of resin, we're adding 5.1 grams of MEKP. The formula weight of MEKP is ~210, so the mole fraction of the 5.1 grams MEKP added to the 1,000 grams of resin is ~0.0242. Using this and the 77°F boiling point pressure for MEKP from Figure 2 (23.184" HgV gauge), the ideal gas laws yield a potential of ~2.63 liters (160 CI) of evolved gas.

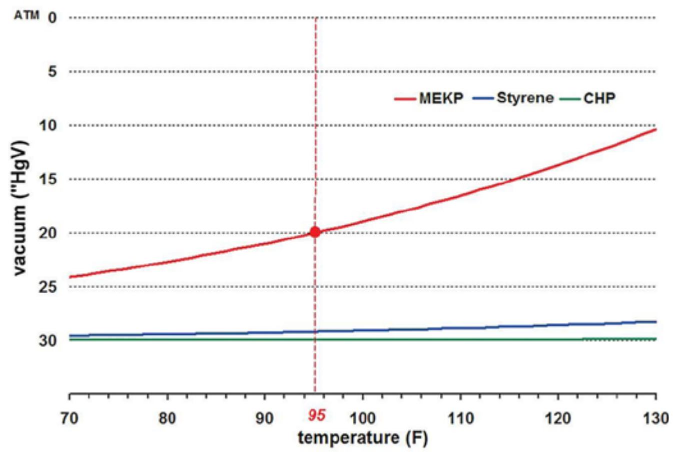

Figure 3. Infusion Area Phase Coexistence Lines

So, does this mean MEKP can't be used in the infusion process? No. Just how prevalent the evolution of gas is in any given system depends on a number of factors. These range from the resin chemistry and – like the glycol mix in your car's radiator – its effect on the boiling point of the MEKP to free radical species evolution and crosslinking during the reaction. Another factor is the selected laminae and its ability to nucleate bubble formation, like Mentos to Diet Pepsi. The point, however, remains the same: it doesn't take much of a low-boiling compound to create a huge void content problem.

A word of caution: we moved to "pure" CHP as the initiator of choice for the application of interest, as the peroxide plays a critical role in the formation of the thermoset and ultimately its physical and mechanical properties. But the decision was made under the guidance of the resin manufacturer. Therefore, as you design and produce your next part, don't be afraid to seek out the wealth of knowledge available from your supply chain.