

# VARIABLE CATALYST INJECTION RATE FOR CYCLE TIME REDUCTION IN LIQUID COMPOSITE MOLDING

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**SUMMARY:** The objective of this work was to investigate techniques of shortening the cycle time in liquid composite molding. In order to accelerate the cure reactions, elevated mold temperatures and heated injection streams were used. However, the incoming resin temperature was lower than the mold temperature and this resulted in a mold quench effect near the resin inlet. The lower temperatures near the inlet resulted in a slower cure that limited the cycle time. A variable catalyst injection strategy was employed in an effort to counter the delay from the mold quench. Liquid molding experiments were performed on preforms consisting of all continuous strand mat (CSM) or all fabric plies using the variable catalyst strategy. With the CSM preforms, the variable catalyst strategy was found to be effective at countering the mold quench near the inlet. However, with the fabric preforms, success was very limited due to the dual scale porosity of the preform. The dual scale porosity led to the dispersion of the resin throughout the mold and an inability to concentrate highly catalyzed resin in the inlet region affected by the mold quench.

**KEYWORDS:** cycle time reduction, variable catalyst injection, dual phase porosity

## INTRODUCTION

Liquid composite molding (LCM) has been touted as a process with the potential to reach production volumes of up to 30,000 parts per year with a single tool [1]. By aerospace standards, 30,000 parts per year is high volume but it is a relatively low volume by automotive standards. In order to gain more widespread acceptance as an automotive lightweight material, significant productivity improvements would be necessary. A key to reaching shorter cycle times would be the use of higher molding temperatures that drive the curing reactions to completion more quickly while still providing ample time to fill the mold prior to resin gelation.

One of the challenges of optimizing a non-isothermal LCM process is managing the large temperature gradients that can result from the resin injection phase. Typically, these temperature gradients result from injecting a lower temperature resin into a higher temperature mold. Near the resin inlet, the cooler resin absorbs heat from the preform and carries that heat along into the mold. As the resin injection phase proceeds, a constant flow of lower temperature resin passes through the inlet region of the mold effectively quenching that region from the original mold

temperature down to the resin inlet temperature. This “mold quench” effect near the inlet results in lower resin temperatures and slower reaction kinetics. As a result, the cure time of the resin near the inlet area is often the limiting factor in determining the cycle time of the part. Modeling the simultaneous resin flow and heat transfer that leads to mold quench has been treated both analytically [2] and numerically [3-4].

Researchers have tried various process modifications to reduce the cycle time increase due to mold quench. A mold design with a heating zone localized in the inlet region has been proposed [5]. The inlet region was pre-heated to a higher temperature than the surrounding mold to compensate for the mold quench. In another approach, a microwave resin preheating system was implemented to heat the incoming resin [6]. Here, the last resin into the mold could be preheated to a higher temperature to overcome the mold quench effect. Variable catalyst injection is another strategy that has been proposed to offset mold quench [7, 8]. By increasing the concentration of catalyst injected near the end of fill, the chemical reactivity of the resin residing in the mold quench region is increased. A highly catalyzed resin system at a lower temperature could potentially react as fast as a less catalyzed resin at a higher temperature.

A potential problem with the variable catalyst approach is its reliance on the plug flow assumption during mold filling. This approach implicitly assumes that the first resin injected into the mold will be pushed to the back of the mold and that the last resin injected will reside in the inlet region. Deviations from this filling pattern can result when the local resin velocity in the mold differs from the average resin velocity. Experimental results based on measuring thermal dispersion during the mold fill [9] have indicated that local resin velocity variations cannot be neglected in modeling temperatures within the mold.

Resin velocity variations in a mold can be large when the preform has a dual scale porosity [10] typically found in fabrics. Dual scale porosity refers to differences in flow resistance within a fiber tow versus the flow resistance between tows. Flow between tows is preferred so that the resin front between tows advances faster than the flow front within the tows leaving an unsaturated length of tow. Although this dual scale porosity phenomenon has been studied extensively in the literature [11, 12], its full effect on local resin velocity within the mold is not completely understood. Conceptually, the resin flow can be thought of as higher than average axially throughout the flow channels between tows and effectively zero within the tows. A fraction of the resin flowing between tows eventually is pushed aside into the tow where it essentially stops. Because of the wide dispersion in resin velocities within the mold, fabric based preforms are expected to pose a formidable challenge to the variable catalyst strategy.

The objective of this work was to explore the variable catalyst injection strategy towards shortening LCM cycle time. More specifically, the effectiveness of the variable catalyst injection was evaluated on both fabric based and continuous strand mat based preforms in an effort to determine the effect of dual scale versus single scale porosity.

## **EXPERIMENTAL**

### **Materials**

A low viscosity epoxy resin system was used for all of the experiments. It was a three component system consisting of an epoxy resin (DER 383 from Dow Chemical), an anhydride (MTHPA 600 from Lonza), and an imidazole catalyst (either 2-4 EMI or dimethylimidazole,

DMI, from Aldridge). A constant mix ratio of epoxy to anhydride of 100:80 was maintained throughout but the catalyst and concentration were varied. Two different fiber reinforcements were used. A continuous strand mat (8610 CSM from Owens Corning) and a plain weave fabric 2454 from Fiber Glass, Inc. (FGI).

## Molding Equipment

The resin injection system was a three-stream dispensing unit. Precise flow rates of each stream were insured via a computer controlled hydraulic system consisting of coupled hydraulic cylinders. Accurate LVDTs were used to monitor the displacement of the piston for each stream. Temperature control of the dispensed resin was achieved via heating jackets around the resin cylinders and heat tape on the flexible lines leading to the static mixer.

A steel mold with a 44.5 cm square cavity and a thickness of 3 mm was used for all moldings. The mold was instrumented with pressure transducers, thermocouples, and dielectric cure sensors to facilitate process monitoring. A perimeter O-ring enabled the mold to be evacuated prior to molding. Fig. 1 presents schematic diagrams of both the resin dispensing unit and the mold.

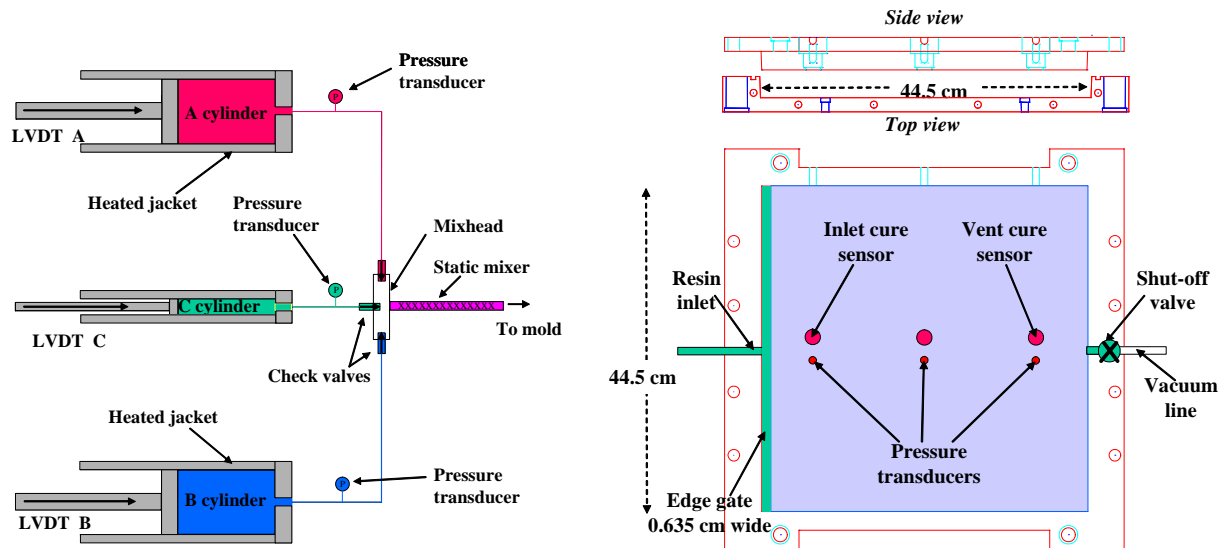


Fig. 1 Schematic diagrams of the resin dispensing unit and of the steel mold.

## Molding Process

All of the molding experiments followed the same process. Firstly, the glass fiber preform (5 plies of 2454 fabric or 4 plies of 8610 CSM) was placed into the mold leaving a 6.3mm gap along the inlet mold wall. This gap served as a resin runner in an effort to get a linear flow front across the entire mold width. The mold was closed and preheated to 145°C. The epoxy stream was preheated to 105°C and the anhydride stream to 70°C in an effort to match the respective viscosities at the mix head and end up with an 80°C mixture. The mold and the resin streams were allowed to reach thermal equilibrium prior to molding. The mold was then evacuated via a vacuum line on the vent and the resin injection was initiated. After 10 s, the shut-off valve at the mold vent was closed and at 20 seconds, mold filling was complete and the inlet shut-off valve was closed.

## RESULTS AND DISCUSSION

### Mold Quench Effect with Uniform Catalyst

With the baseline molding conditions of a 20 s mold fill of an 80°C resin into a 145°C mold, the effect of mold quench was observed with a set of sacrificial, thin gauge thermocouple wires. These wires were introduced through the mold vent and extended various distances into the mold. As seen in Fig. 2, a 20°C temperature drop was measured at a point 7.5 cm from the inlet while points further from the inlet showed very minor temperature drops. The effect of this mold quench was observed in the cure profiles as measured by the inlet and vent dielectric sensors. Plots of the log ionic viscosity ( $\text{Log}[v_i]$ ) vs. time [13] are shown in Fig. 3. The mold quench effect has resulted in 25 s delay between vent and inlet cure profiles.

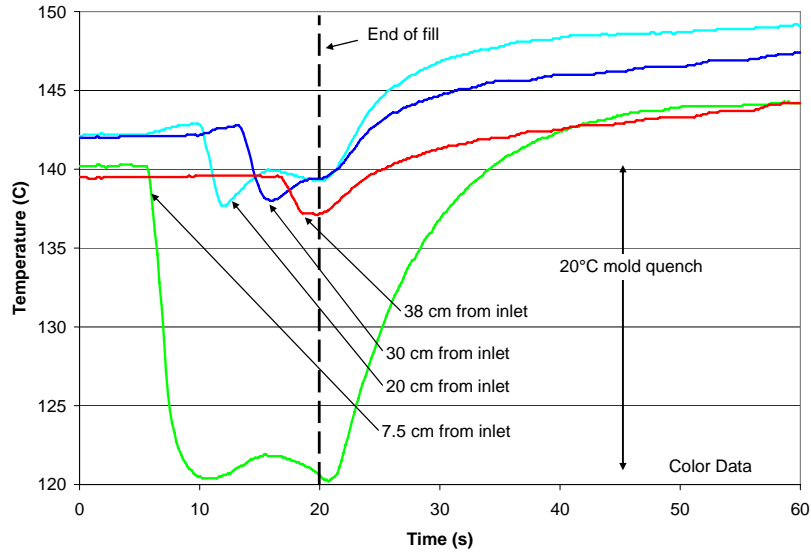


Fig. 2 Temperature as a function of time showing mold quench.

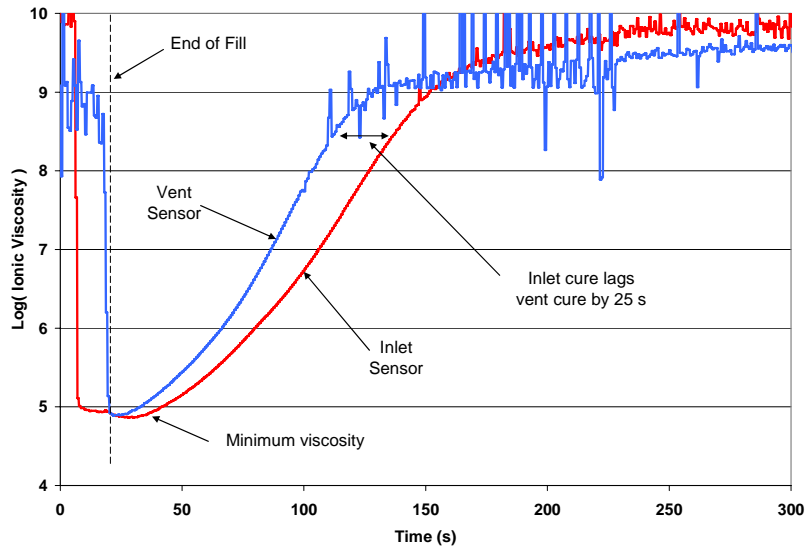


Fig. 3 Cure profiles with constant catalyst.

## Variable Catalyst Injection Molding Results

A series of moldings were made in which the 20 s injection was divided equally between an initial low catalyst concentration and a subsequent high catalyst concentration resin. For molding the fabric preform, the initial resin contained 1.5 phr DMI and was increased to 3 phr DMI for the second half of the injection. The cure profile at the inlet and vent from this molding are compared to those from a constant 2 phr DMI resin injection in Fig. 4. For the RTM molding into the CSM preform, two variable catalyst injections were performed: one used 1 phr EMI initially followed by 3 phr and the second used 2 phr initially followed by the same 3 phr catalyst level. These cure profiles are shown in Fig. 5.

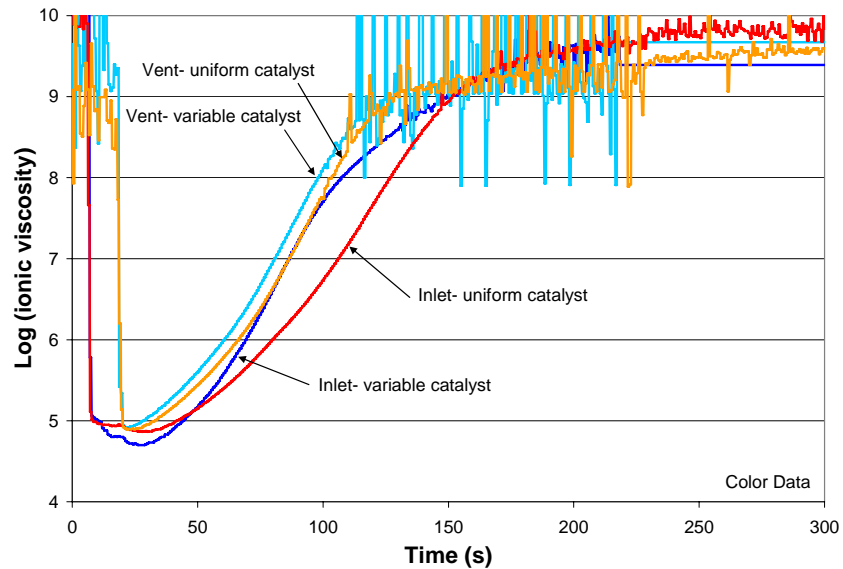


Fig. 4 Variable catalyst/ fabric preform.

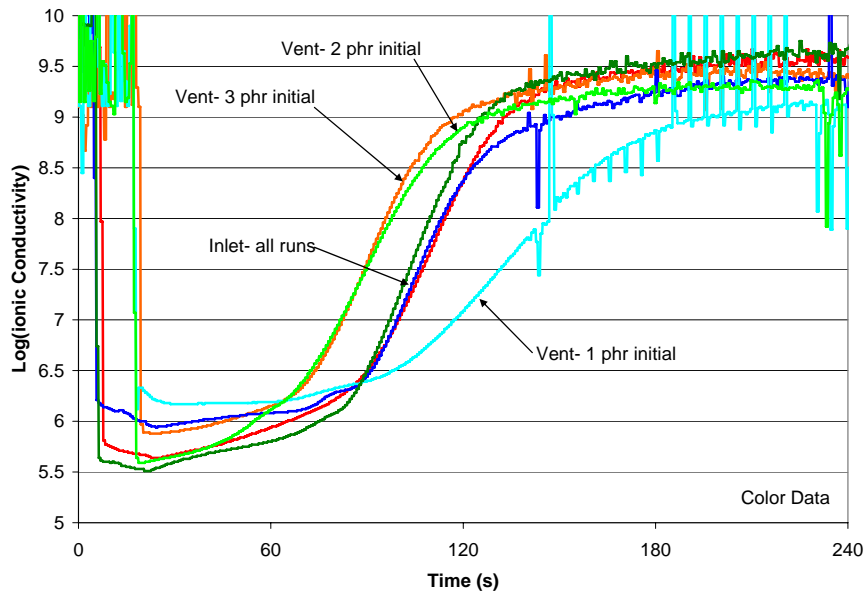


Fig. 5 Variable catalyst/ CSM preform.

Comparing the inlet cure profiles from the fabric perform case (Fig. 4), the variable catalyst injection scheme appears to have succeeded in accelerating the cure near the inlet early in the cure phase, but later in the cure phase the reaction rate appeared to slow down. The net effect was that no significant gain in cycle time was obtained by the variable catalyst injection rate. A possible explanation for the initially faster, then slower reaction rate observed in the inlet region is that the dielectric cure sensor was detecting an average of cure rates from the resin within the tows and the resin between the tows. The resin deposited within the tows was probably catalyzed with only 1.5 phr catalyst whereas the resin between the tows would have 3 phr. In this case, the dielectric sensor would detect the early cure of the 3 phr resin but the lagging cure of the 1.5 phr resin would eventually slow down the measured average.

For the CSM perform, comparison of the cure profiles in Fig. 5 tells a different story. The inlet cure profiles were nearly the same while the vent cure profiles were dramatically different. This data indicates that the flow within the CSM was primarily plug flow. The initial resin containing the reduced catalyst levels was pushed to the back of the mold (vent side) while the second half of the resin catalyzed to a constant 3phr was confined to the inlet area.

### **Delayed Catalyst Injection Molding Results**

In an effort to highlight the differences between the dual scale porosity in fabrics and the single scale porosity in CSMs, the variable catalyst experiment was taken to an extreme case. In these moldings, the first third of the total resin volume was injected with no catalyst. Uncatalyzed resin will take hours to cure instead of minutes for the catalyzed systems. Rather than subtle differences, the final location within the mold of the uncatalyzed resin was expected to have a strong effect on the measured cure profiles.

The cure profiles for the fabric perform are shown in Fig. 6. In this case, the inlet cure profile was dramatically slower while the vent cure profile was barely changed. The uncatalyzed resin must have flowed into the glass tows near the inlet and stayed put while the catalyzed resin that followed must have flowed past in the channels between tows. The cure profiles for the CSM perform shown in Fig. 7 are vastly different. Although the inlet cure profile is delayed slightly from the baseline case, it is the vent cure profile that is dramatically different. In fact, during the data collection period, no evidence of cure was detected at the vent sensor. Clearly, the uncatalyzed resin must have been pushed toward the mold vent. The minor delay observed at the inlet sensor indicated that a small quantity of uncatalyzed resin remained near the inlet

## **CONCLUSIONS**

These results have strong implications for the potential application of variable catalyst injection strategies. For CSM based preforms, the plug flow filling pattern enables the use of a variable catalyst injection to reduce cycle time. Low axial dispersion of resin permits a faster reacting resin to be concentrated near the inlet. However, for fabric based preforms, the variable catalyst injection strategy is expected to have limited success due to the wide axial dispersion of the resin resulting from the dual scale porosity.

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