ADVANCED THERMOSETTING RESIN MATRIX TECHNOLOGY FOR NEXT GENERATION HIGH VOLUME MANUFACTURE OF AUTOMOTIVE COMPOSITE STRUCTURES

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Abstract

Composite materials have gained the attention of the automotive industry to substantially reduce vehicle weight, reduce CO\textsubscript{2} emissions and improve the fuel economy of next generation vehicles. Thermosetting matrix technology combined with glass or carbon fiber reinforcements are well suited for structural applications where mostly steel and aluminum are used today. However, the lack of fast production techniques and fast reacting matrix technologies have limited composites use to low volume production models. A new generation of epoxy resin systems has been developed that allows the rapid processing of structural composites for medium to high volume models. These advanced formulations maintain the excellent properties of traditional epoxy-based composites, yet the tested systems can process in a matter of minutes using modern manufacturing technologies such as the high pressure resin transfer molding (HP-RTM) process. The advanced formulations are unique in that they provide a long enough injection window for a robust impregnation of the reinforcing fibers while still enabling an extremely short cure cycle. The results from this development show that structural composite components can be produced economically and in high volume using today's innovative resin and process technology.

Introduction

Automotive manufacturers, particularly the European premium carmakers, are working vigorously on reducing the weight of their fleets and have begun introducing composite materials on higher volume commercial models. Fiber reinforced plastics using either glass or carbon fibers as reinforcement and thermosetting epoxy resin matrices are an extremely powerful material combination for saving weight in structural applications. As equipment manufacturers have continued to make improvements to the range of composite processes such as prepreg, filament winding, compression and resin transfer molding, resin manufacturers have had to develop new resin systems to compliment these high volume / high speed processes. Requirements include shorter cure time, VOC-free and REACH-compliant systems that do not sacrifice the desirable characteristics of traditional epoxy resins.

This paper focuses on the development of material technology for the resin transfer molding (RTM) manufacturing process which is among the leading technologies for making structural composite parts.\textsuperscript{1} The entire process, as illustrated in Figure 1, requires a short cycle time (< 5 minutes) to be viable for automotive mass production volumes. Today, the main bottlenecks are the manufacture of the preform (Steps 1-2), and the actual injection and cure of the part (Step 4).
Development of Matrix Compatible Preform Binder Technology for Fast Cycle Resin Transfer Molding (RTM) Applications

Today's most economic preforming aids are heat reversible powder binders. These are typically applied to the reinforcement during its manufacturing or shortly prior to the preforming stage (Step 1-2). The binder has the main functions of stabilizing the reinforcements and facilitating the preforming stage without creating other adverse effects. In the case of rapid RTM processing, it is particularly important that there is good compatibility with the resin matrix, the reinforcement’s permeability is not negatively affected and the binder provides enough strength to prevent distortion of the fibers during injection.

Specific epoxy-resin-compatible preform binders were developed to meet these requirements. Table 1 highlights the technical features of these systems. Binder A was developed to be a universal tool for various preforming applications with extended shelf life, a softening temperature between 80 - 90°C, excellent application behavior and good compatibility to RTM epoxy resin matrices. Binder B was developed for more demanding composite process applications, where strong fiber preforms are needed or essentially no fiber deformation is allowed after preforming. This higher level of performance was achieved by means of a “reactive” or “crosslink-able” binder.
Both binders were applied at the rate of 12 grams per square meter (gsm) of surface coverage onto a glass fiber multi-axial reinforcement on top of which carbon fibers were placed for visualizing purposes. The entire preform assembly was consolidated in a press at 120°C and cured (in the case of Binder B). A fast curing RTM resin system (EPIKOTE™ resin 05475 with EPIKURE™ curing agent 05443) was injected using a Cannon ESTRIM™ high pressure RTM machine. The resin was injected at a pressure of 120 bars at 120°C. As shown in Figure 2a, the fibers of the untreated preform were washed away near the central injection port where the flow rates are high. Figure 2b and Figure 2c, stabilized by preform Binders A and B respectively, showed little or no fiber movement. In particular, Binder B caused the carbon fibers to stay in place even at very high fill speeds (up to 200 grams per second) as can be seen in HP-RTM processing.

Fiber distortion in composites is generally to be avoided as it can cause many issues relating to manufacturing, quality and the ultimate properties of the finished part. Especially when combined with high speed injection, high resin viscosities may cause fiber run outs, ply drops, unidirectional fills and low fiber volume. Both binder systems, particularly the crosslink-able epoxy compatible binder, resisted movement of the fibers during resin injection and provided maximum process robustness. Given the additional preform integrity provided by the crosslink-able binder, it is expected that process developers may be able to increase flow / mold fill rates further reducing the time needed for the RTM injection step.
Development of Fast Curing Thermolatent Epoxy Resin Technology for Resin Transfer Molding and Liquid Composite Molding Processes

The cure time required to crosslink the epoxy matrix is one of the key bottlenecks to higher volume composite production. Hence, much attention has been put on so-called “fast cure” systems in recent years. While high end premium or super sport car manufacturers use processes derived from the aerospace industry that only require cure cycles of hours, high volume automotive manufacturing requires cure cycles of minutes or less. At such speeds, the time used for filling the mold and completely impregnating the reinforcing fibers becomes a challenge. Structural composite parts require relatively high fiber volumes of 50% or more. Such parts are difficult to fill particularly when carbon fiber is used. Very low viscosity and having sufficient time for impregnation are the two key characteristics that are needed to achieve quality finished parts. The ideal injection viscosity of a RTM resin should be below 100 mPas for at least 60 second at processing temperature.

In Figure 3, the initial resin viscosity is sufficiently low and remains so for approximately 60 seconds (Step A) which is enough time to impregnate a large part. This impregnation step is followed by a very rapid curing of the resin (Step B) without creating a large exothermic reaction. Step C is the demolding step at which the time the matrix should be almost completely converted.

Conventional fast curing resin systems featuring short cure cycles of 2 to 5 minutes have rheological behavior as indicated by the red reference line. The resin begins to react instantly after mixing. It is difficult to impregnate parts that need time to be filled due to their size or geometry. As a consequence, such parts may come out not fully impregnated, show dry spots or the reinforcements may be distorted since gelation occurs during the injection step (Figure 4). Such fast cure resin systems cannot provide good and consistent part quality.

From these observations it became clear that there was a need to develop not only fast reacting epoxy resin, but resin systems with “thermal latency” that give enough time for impregnation of a large or geometrically complex part followed by a fast reaction.
Figure 3. Rheological Behavior of Conventional and Thermolatent “Fast Curing” Resin Systems.

Figure 4. Carbon Fiber Laminate Using HP-RTM Process and Conventional Fast Curing Epoxy Resin.
Figure 5. RTM Resin Viscosities of 5-minute (System A) and 2-minute (System B) Curing Systems.

Figure 5 shows the viscosity curves of two different and newly developed fast curing RTM resin systems. RTM resin System A (EPIKOTE™ resin 05475 and EPIKURE™ curing agent 05443) fully cures within 5 minutes at 120°C. RTM resin System B (EPIKOTE™ resin 05475 and EPIKURE™ curing agent 05500) fully cures within 2 minutes at 115°C. As seen from the figure, both systems have very low and almost constant viscosity at the recommended curing temperatures for 60 seconds. System A provides a bit more latency while System B requires a higher level of temperature and process control during the molding cycle to guarantee full cures.

Figures 6 depicts a typical HP-RTM injection cycle for conventional fast curing RTM resin system as compared to novel resin System A. The in-tool injection pressure remains low during the mold filling cycle confirming the very low viscosity and latency of the system. The conventional fast curing system leads to a substantial pressure increase even during the very short fill times of 10 seconds. As a result, the part is not sufficiently filled and the preform distorts due to its rapid viscosity build (also Figure 4).
Figure 6. HP-RTM Injection Cycle for Novel Resin System A vs. Conventional “Fast Curing” RTM Resin. The in-mold injection pressure remains low during the mold filling cycle.

Cost Considerations

Cycle time (fast curing) is also an important factor to the total cost of a part and is relevant to the number of parts that can be produced from a single tool in a given time period. To meet annual volume demands, a manufacturer may require multiple sets of tools adding significantly to the investment and part cost. A number of studies have compared the cost of composites to that of steel and other automotive materials. With the advent of new composites processing equipment and resin systems, however, most of these studies are outdated with respect to the assumptions used for composite cycle times. Therefore, previously-held notions about the viability of composites for high(er) volume production should be reconsidered.

Table 2 shows the annual volume that can be attained on a single tool as a function of cycle time. A cycle time of 3 minutes (1 minute of injection and 2 minutes of cure time), for example, could support production of up to about 68,000 parts per year. At a volume of 35,000 parts per year, the total cost of a carbon fiber hood outer panel ranges from $70 - $100 each depending on the cycle time. The carbon fiber itself makes up 85 – 90% of the total part cost and is the most significant cost component. However, reducing cycle time decreases the number of tools required, and therefore, the total cost of the part by up to 27%. Figure 7 shows the effect of reducing cycle time on the total cost of the part.
### Table 2: Annual Attainable Volume Using a Single Tool as a Function of Cycle Time

<table>
<thead>
<tr>
<th>Part Cycle Time</th>
<th>17 minutes</th>
<th>10 minutes</th>
<th>5 minutes</th>
<th>3 minutes</th>
<th>1 minute</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annual Attainable Volume*</td>
<td>12,000</td>
<td>20,400</td>
<td>40,800</td>
<td>68,000</td>
<td>204,000</td>
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*Assumes 2, 8-hour shifts @ 5 days/week, 50 weeks/year @ 85% utilization

### Conclusions & Summary

New preform binders, including a crosslink-able system, enable higher volume production of lightweight composites by maintaining fiber placement under high injection pressures and speeds. In tandem, new epoxy resin systems have been developed that offer a unique combination of improved flow and thermolatent cure characteristics that allow fast overall cycle time without sacrificing proper resin filling of large or geometrically complicated parts. RTM epoxy system cure times are below 5 minutes and can be shortened to two minutes in combination with new high pressure RTM molding equipment. With carbon fiber composites, the cost of carbon fiber itself is the major contributor to total cost. However, reduced cycle time epoxy resin systems can also have a significant impact on reducing total part cost and should not be neglected.

*Momentive Specialty Chemicals develops and manufactures products for enabling fast cycle time molding of composites including fiber sizing for glass and carbon fiber reinforcements, preform aids, resin systems and additives.*
References


