HIGH TG FAST CURE RESIN SYSTEM

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ABSTRACT

A quick cure high glass transition temperature (Tg) resin system designed for fast ramp rate cures up to press molding conditions is discussed. The resin system is able to fully cure within 10 minutes at the dwell temperature of 163°C and a demold time of just 2 minutes, even when fast ramp rates are used. The material has been shown to withstand temperatures needed for the automotive electro-coat with subsequent cures to apply the primer and topcoats while maintaining a class “A” finish. Once cured the material also has the ability for post machining and workability. The new CFRP material also has excellent mechanical properties allowing it to be used in structural areas. Due to the quick cure cycle, excellent mechanical properties, broad range of UD and fabrics, and high Tg of this CFRP, a broader use of carbon fiber composites both in the automotive and industrial industries will be seen for both structural and non-structural use.

1. INTRODUCTION

As tougher emissions standards imposed by the 2025 US corporate average fuel economy and European CO_2 requirements come into effect on the automotive industry[1,2], the use of exotic materials has been increasing in recent years. Aluminum has been adapted and used by most of the automotive companies due to the ease of transition and similar manufacturing techniques to that of steel. Carbon fiber composite parts can improve the weight savings while also having the highest stiffness to weight ratios of any material. One way of doing this is to use the material in specific areas in the BIW (Body in White) that need the high stiffness of the CFRP. Due to the challenges and the cost, full scale use of the material will be slow to incorporate. However, integration of CFRP into the “body in white” for key areas where stiffness and weight reduction is needed has already begun. The challenge will be the ability to coat these parts effectively during the inline process, along with the rest of the materials. Automotive companies will need to coat the entire BIW with an electro-coat (e-coat) to protect the metal parts from corrosion. Even though corrosion is not a problem for the CFRP parts, they must be coated at the same time and thus be able to withstand the very high curing temperatures of the E-Coat, primer, topcoat, and clear coat that can reach temperatures up to 180°C. This inline process is already being used to decrease the manufacturing costs of the vehicle. By avoiding the offline coating and subsequent part attachment decreases the cost of production for CFRP parts and allows for a more consistent coating throughout the vehicle. Many snap cure products have been made for the automotive industry but the glass transition temperatures (Tg’s) of these materials have been below 160°C, not making them ideal for the cure cycle of the coatings used on the BIW. These materials are usually coated offline and assembled after the paint booth stage as is done with Toray’s existing G-83C products. This does not make it ideal to use and increases the steps to assembling the BIW. Furthermore many of the current resins used for carbon fiber have high shrinkage after the cure creating read through of the fiber to surface, making it difficult to create a class “A” surface.

2. EXPERIMENTATION

2.1 Cure Kinetics

An Alpha Series Dynamic Mechanical Analysis machine was used to determine the time for the matrix to reach the full torque response of the resin which is called the S' and can be used to correlate a degree of cure. The S' was measured by increasing the temperature at 50°C/min to a final temperature of 163°C. The maximum S' value was determined by allowing the material to cure for 30 minutes and then finding the maximum point and using this time to be the full cure time for this temperature. This maximum was normalized to be 100. This technique was used to determine the latency of the resin during the temperature ramp and can be used in conjunction with DSC to determine the degree of cure.

2.2 Rheology Study

The rheology of the resin was measured using a dynamic viscoelasticity measuring device (Rheometric Scientific ARES-M) using parallel plates with strain of 10%, frequency of 0.5Hz, plate gap of 1.0mm, and plate diameter of 40mm using dynamic temperature ramps of 2°C/min. The resin system needs to have a suitable viscosity for processing and handling while still being able to flow at higher temperatures.

2.3 Dynamic Mechanical Analysis (DMA)

Thermal evaluation was carried out using a TA Instruments Q800 DMA with a standard dynamic temperature ramp of 5°C/min with a frequency of 1Hz on cured composite to determine onset glass transition temperature (Tg). Tests were carried out according to ASTM D7028, Standard Test Methods for Glass Transition Temperature (DMA Tg) of Polymer Matrix Composites by Dynamic Mechanical Analysis (DMA). Specimen Dimension was 55mm length by 12mm width by 2.6mm thick.

2.4 Mechanical Properties Performance

Autoclave panels were cured at 163°C for 10 min., at a ramp rate of 2.8°C/min and an applied autoclave pressure of 0.59MPa. A standard bagging method was used prepare the coupons. The mechanical test evaluation plan is shown in Table 1.

Table 1. Mechanical test evaluation plan.

Test Panel	Test method	Test Condition	
0° Tension Strength and Modulus (Poisson's Ratio)	ASTM D3039	$[0]_6$	RTD
90° Tension Strength and Modulus	ASTM D3039	$[90]_6$	RTD
0° Compression Strength and Modulus	ASTM D695	$[0]_6$	RTD
V-notch IPS	ASTM D5379	$[0/90]_{4S}$	RTD
Short Beam Shear (SBS)	ASTM D2344	$[0]_{12}$	RTD
Flexural Modulus	ASTM D790	$[0]_{12}$	RTD

2.5 Post Cure to simulate Coating

The part was cured in a mold at 163°C for 10 minutes in an oven under vacuum pressure. Once the part was cured and demolded pictures were taken to show the smoothness of the part and the ability to create a good surface finish even when using fabric. The part was then placed into an oven at 200°C for 2 hours to simulate worst case scenario for curing an E-coating onto a part along with subsequent cures from applying the primer, topcoat and clear coat. Pictures are in Figure 8 and show that resin shrinkage had not occurred.

3. RESULTS

3.1 Cure Kinetics

The epoxy snap cure system is able to achieve a high degree of cure within a time period of approximately 10 minutes after reaching set point temperature as shown in Figure 2 below. This epoxy snap cure system can be demolded in as little as 2 minutes after reaching a dwell temperature of 163°C where it reaches 60% of its total torque and has a percent cure greater than 90% using DSC. The epoxy snap cure system also shows good latency at the lower temperatures allowing for good resin flow which allows it to fill areas of the mold cavity and to fully wet out the fibers even when using very fast ramp rates. Shorter dwell times may be possible and will be studied in the future. Press molding or isothermal conditions may need slightly longer times since there is no ramp for this process.

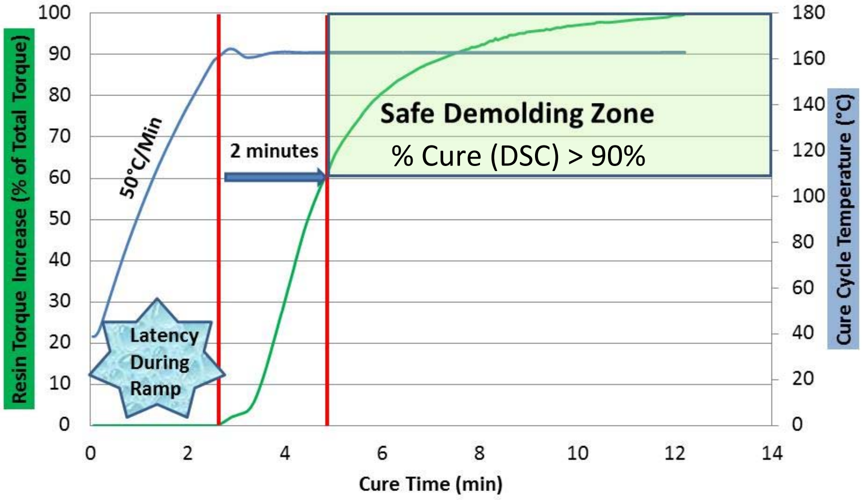

Figure 2. Torque increase of resin (S') with a fast ramp rate cure at 163°C

3.2 Rheology Study

The epoxy snap cure system shows a longer induction time and lower viscosity compared to conventional resin systems as shown in Figure 3. This long induction time at lower viscosities will allow the resin to flow faster and longer where resin is needed to fill dry areas of the tooling and fibers quickly before the gel starts, allowing for faster ramp rates. Even though the induction time is longer the cure rate is quicker making the overall cure time very short as shown in section 3.1. This particular system was designed to achieve a minimum viscosity with enough catalyst latency to allow for adequate flow during the cure. The use of fabric reinforcement further exacerbates the need for a resin system that can flow in and around the weave.

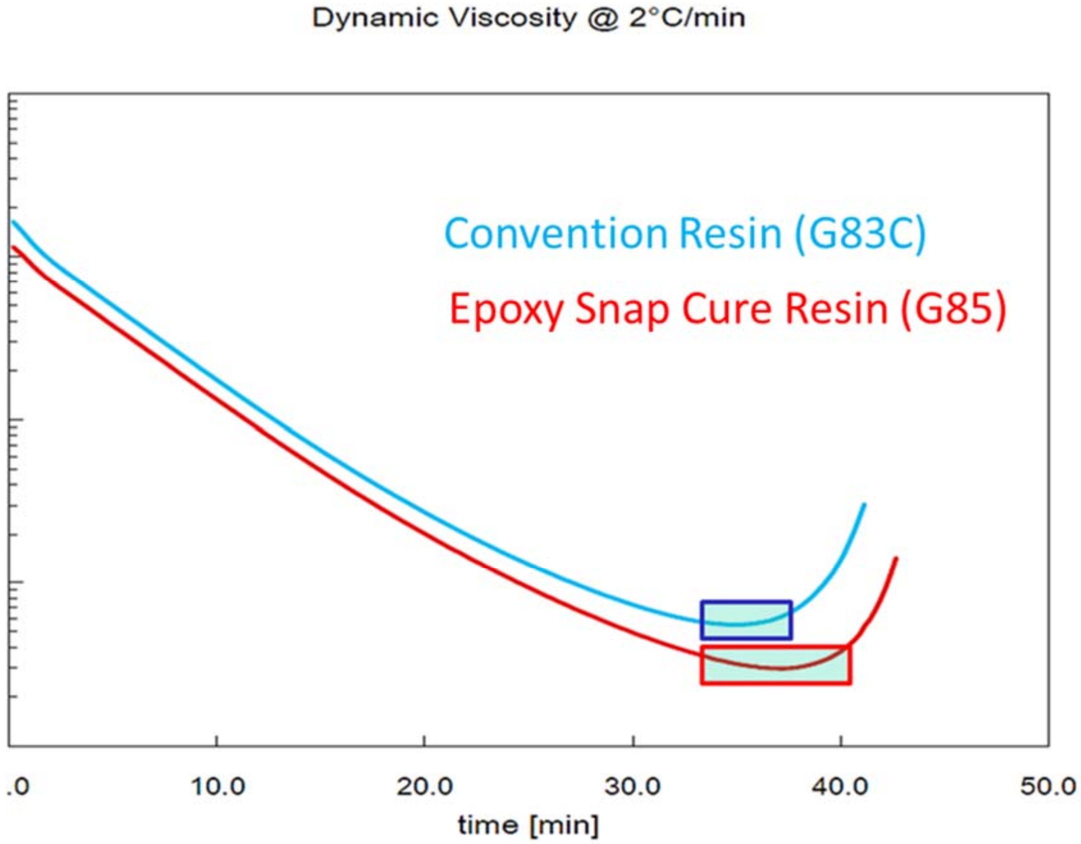

Figure 3. Rheology Profile at 2°C/min

3.3 Dynamic Mechanical Analyzer (DMA)

The onset glass transition temperature (Tg) was measured using a TA instruments dual cantilever DMA. The test was run from 25°C up to 275°C with a ramp rate of 5°C/ min at 1 Hz per ASTM D7028. The test sample was conditioned at room temp for 40 hours before testing. The G' onset Tg is 177°C and is shown in Figure 4.

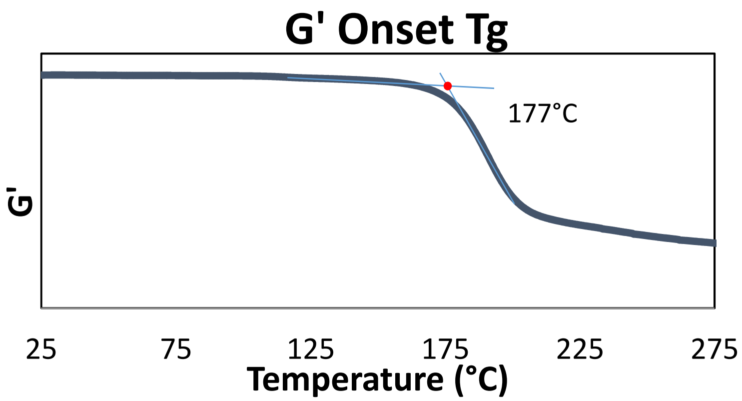

Figure 4. Graph of G' onset Tg in Degrees Celsius

3.4 Mechanical Properties

Mechanical properties G85/T700S-60E were tested per the applicable ASTM standards. Relative values of G85 to G83C mechanical properties are shown in the radar chart of Figure 5. G83C has slightly lower mechanical properties but has the advantage of curing at lower temperatures for parts that do not need the higher Tg's. Additional mechanical testing were performed using T300B 2x2 Twill and T700S-60E and shown in Table 2.

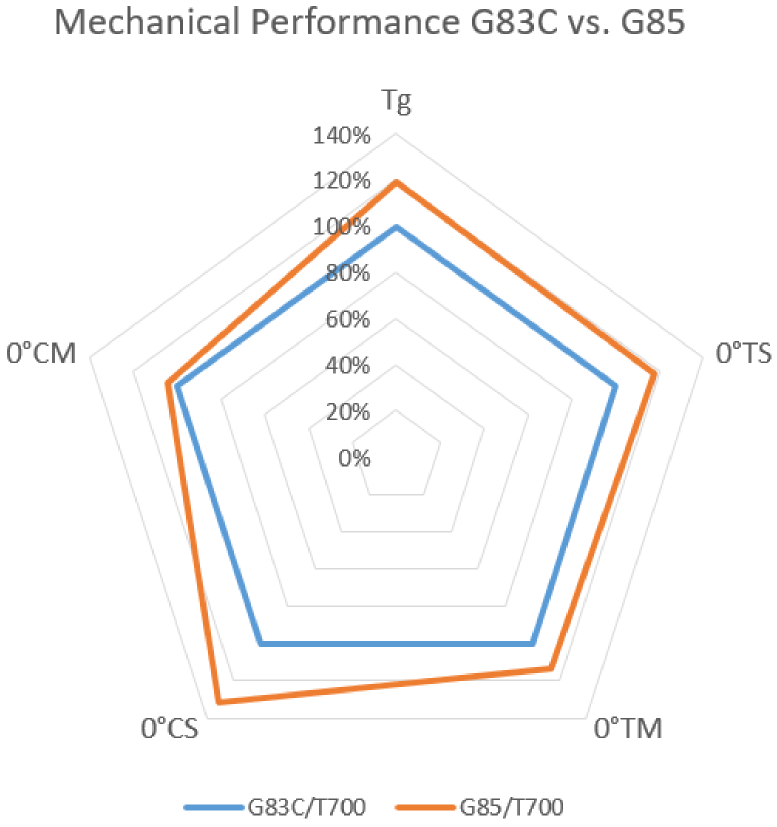

Figure 5. Mechanical Performance of G83C vs. G85

Table 2. Mechanical Test Results of T300 fabric vs. T700 unidirectional prepreg

Resin			G85*	G85**
Rc % by weight			42%	37.5%
FAW g/m2			204	190
Fiber / Fabric weave			T300B-3K / 2X2 Twill	T700S-60E
Property	Unit	Method		
DMA Tg	°C	ASTM D7028	177	177
0° TS	MPa	ASTM D3039	606	2680
0° TM	GPa	ASTM D3039	57	130
90° TS	MPa	ASTM D3039	600	-
90° TM	GPa	ASTM D3039	57	-
0° CS	MPa	ASTM D695	-	1667
0° CM	GPa	ASTM D695	-	112
V-notch IPS	MPa	ASTM D5379	90	-
ILSS	MPa	ASTM D2344	12	-
Flex. Mod.	GPa	ASTM D790	83	-
Poisson's Ratio	--	ASTM D3039	0.05	-
*Values Normalized to $V_f = 49\%$ ** Values Normalized to $V_f = 54\%$				

An example part using G85/T300B 2x2 Twill is shown below in Figure 6. With proper layup techniques and tool preparation the part can maintain a class "A" finish without sacrificing distinctness of image or telegraphing of the fabric from the resin shrinkage due in part to the design characteristics of the epoxy snap cure resin matrix.

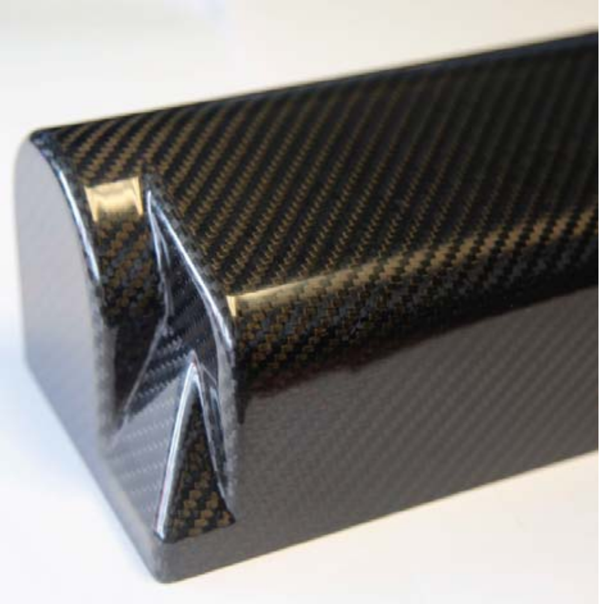

Figure 6. Surface Finish of the epoxy snap cure resin with T300 2x2 Twill (no clear coat used)

3.5 Post Cure to simulate Coating

The results of the post cures to simulate the coating process showed no shrinkage of the resin that would normally create telegraphing of the fibers through the resin and making it difficult to create a smooth finish during the coating process. Figure 7 shows that there is not any significant telegraphing of the fibers and there is a good overall distinctness of image from the reflections of the pens.

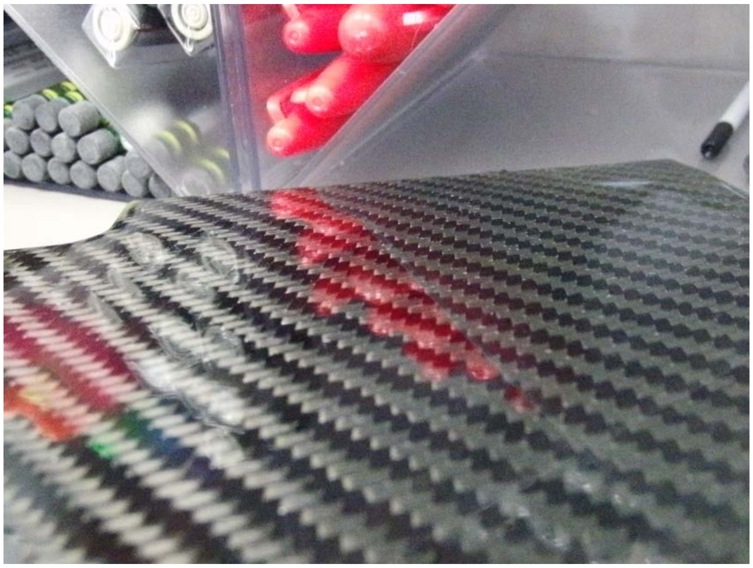

Figure 7. Image of 2X2 twill surface finish after curing in the mold and before post cure

After the post cure at 200°C for 2 hours the material was photographed again to see if there were any reduction in surface quality. From Figure 8 we cannot see any significant difference in the surface quality from that of the pre post cured part.

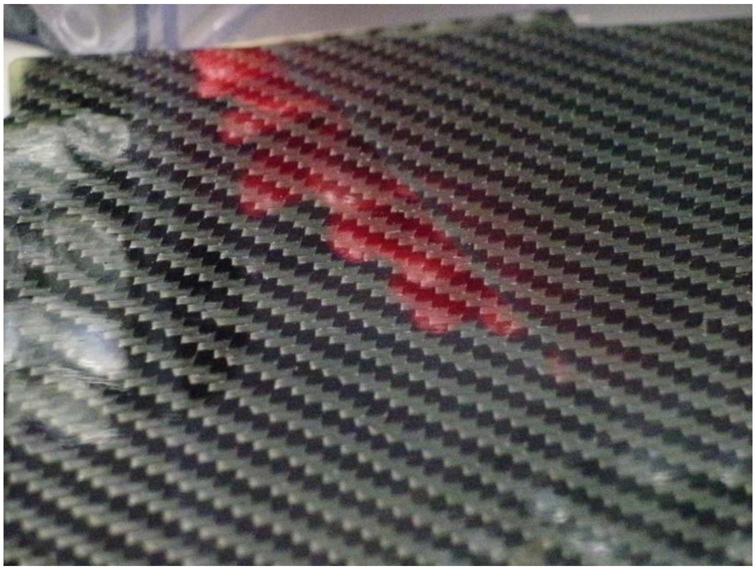

Figure 8. Image of CFRP 2x2 twill after 200°C 2 hour post cure

4. CONCLUSIONS

The need for CFRP lightweighting is increasing as automakers struggle to meet the future 2025 CAFE standards[1] and the European CO_2 requirements for new cars and light-commercial vehicles[2]. The use of epoxy based carbon fiber reinforced composites in the automotive industry creates many challenges to implement. The high formability, extremely high strength to weight ratio and being one of the lightest materials that can be used for structural parts makes these challenges worth tackling. Due to these challenges and the cost, full scale use of the material will be slow to incorporate. However, integration of CFRP into the "body in white" for key areas where stiffness and weight reduction is needed has already begun[3]. This challenge has been met by the new epoxy snap cure resin and has shown the ability to coat these parts effectively during a mock inline process. The manufacturing cost can decrease coating the CFRP parts inline. With epoxy snap cure resin's ability to demold at 2 minutes and to achieve full properties during the painting process or subsequent post cures makes it viable for high production rate vehicles.

Toray currently has an epoxy snap cure resin system in the automotive market being used for both structural and cosmetic parts that hopes to solve the above problems. The material branded G85 has a Tg of 177°C allowing it to be processed at the higher cure temperatures of the coatings used in the automotive industry. The CFRP was exposed to a temperature of 200°C to simulate the E-coat curing process and showed no deformation or shrinkage of the resin. This maintained the class "A" finish with little to no telegraphing of the fibers through the resin, allowing it to be easily coated. Toray is currently working with automotive coating companies to further study the painting process with the intent to benefit the parts manufacturers.

Along with the resistance to warpage during the coatings cycle the epoxy snap cure resin system named G85 also has excellent mechanical properties that are high enough for structural parts as well as cosmetic. The quick cure system also allows the material to be processed timely without increasing the overall time to process. Many cure cycles can be used and can be verified and adjusted as needed for the customer.

5. REFERENCES

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