

# LOW TEMPERATURE CURE POLYURETHANE ADHESIVE FOR “PRIMERLESS” COMPOSITE BONDING

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## Abstract

Two-part polyurethane adhesives have long been successfully utilized within the transportation industry for bonding sheet molding compound, SMC, for both interior and exterior body panels. Historically, high volume production rates necessitated the use of heated bond fixtures to ensure minimum button to button cycle times. The drive to reduce overall composite part cost and the shift to lower volume applications has led to a number of changes and is forcing still others. Among these is a shift away from costly heated bond fixtures, paint bake temperature reduction and a swing from more traditional SMC composite to hand spray up, HSU, and resin transfer molding, RTM, processes. While not new to the industry, these alternate composites typically require surface preparation such as sanding, priming or both to obtain specification passing bond results; all of which add cost. One option is to move to acrylic adhesive technology, but this limited by its regulation as a flammable substance and nuisance odor. A new polyurethane adhesive has been developed that provides excellent adhesion to SMC, HSU and RTM without surface preparation requiring only a room temperature cure or greatly reduced post bake temperature. This presentation will review the historical processes, the drivers for change, and test data for the new polyurethane adhesive PLIOGRIP 8400/ 8605.

## Introduction

Driven primarily by weight reduction, part consolidation and short cycle times, sheet molding compound, SMC, has a long history of use within the transportation industry including automotive, heavy truck and marine. The SMC process requires a sizable up front investment to initiate production. Mixing and filming of the compound is required prior to molding under heat and pressure. Typically the mold is made from machined steel or cast alloy and may be hardened or chromed for durability. A typical molding cycle may range from 1 to 5 minutes easily producing 25,000 parts per year using just one production shift. In many applications these components require adhesive bonding to provide a finished article for commerce. In order to keep up with the rapid molding pace, automated bond fixtures have been introduced to robotically apply adhesive, mate components and apply heat to accelerate adhesive cure. This process is typically followed by a primer and or top coat application with post bake at elevated temperature, all adding yet further capital cost. Figure 1, shows the SMC process from compounding, charge placement, molding and finally robotically applied adhesive application. For high volume applications this process has been quite successful. However, customers continue to demand cost reductions while also reducing annualized volumes. Prime targets for cost reduction include elimination of heated bond fixtures, reduction of paint oven temperatures, and a shift to lower cost, lower volume molding processes such as resin transfer molding, (Figure 2), and hand spray up, (Figure 3). These process shifts are not new to the industry but are again growing in number.

The resultant composite from HSU and RTM processes have on occasion presented challenges for heat cured polyurethane adhesives and more of a hurdle for room temperature cure processes. These obstacles have generally required surface abrasion, chemical priming or both to achieve appropriate adhesion, both of which add cost. One alternative is to utilize a 2-part methyl methacrylate adhesive. Methyl methacrylate-based adhesives have a successful history bonding HSU in both the marine and transportation industries. However, their selection is accompanied by several trade-offs including higher cost, nuisance odor, flammability, volatile organic compounds (VOC's), and short shelf life of the peroxide initiators.

This paper will review the performance of a typical polyurethane adhesive and demonstrate how the new technology overcomes existing hurdles that may lead to reduction in capital investment and processing costs.



Figure 1: SMC Raw Material to Finished Product



Figure 2: RTM Light, or Vacuum Molding



Figure 3: Hand Spray Up Process

Lap shear test coupons were prepared according to ASTM D 5868 and evaluated at listed temperatures using a loading rate of 13mm/min, see Figure 4. All lap shear values listed represent an average of five samples. Isopropyl alcohol, IPA, or methyl ethyl ketone, MEK, wipes were prepared by applying solvent to a clean paper towel and wiping the surface three times. IPA is widely used in the industry for removing dust and dirt prior to adhesive application. Solvents were allowed to flash off for five minutes after which the adhesive was applied. PLIOGRIP® 6031/6032 2-part epoxy primer was applied using a single wipe of an impregnated paper towel. The primer was also allowed to flash off for five minutes prior to adhesive application. Scuff sanding was performed with several hand held passes using 80 grit sand paper. The surface was then wiped with IPA, to remove dust prior to adhesive application. Substrates were obtained from a number of well-known composite molders as well as Ashland Inc.

Cross peel testing was conducted according to SAE-1553 but modified to heat the uncured specimen within the fixture and test the sample at temperature immediately following without allowing the samples to cool, see Figure 5. Cure temperatures ranged from 22°C to 149°C as listed. Cross peel data was generated exclusively over electro-coated steel to remove substrate as a variable. Values listed represent an average of three samples.



Figure 4: Lap Shear Test



Figure 5: Heated Cross Peel Tester

The adhesive was loaded into 1:1 200 ml side by side cartridges and applied via a pneumatic dispense gun using a 3/8 x 30 static mixer. The material may also be applied using conventional meter-mix equipment.

## Definitions

Definitions used in this work include the following:

kPa = Kilopascals, 1 psi = 6.89 kPa  
RTM = Resin Transfer Molding  
MEK = Methyl Ethyl Ketone  
FT = Fiber Tear

SMC = Sheet Molding Compound  
IPA = Isopropyl Alcohol  
LSS = Lap Shear Strength  
VOC = Volatile Organic Compounds

**60C Lap Shear Test Over SMC Following 72 Hour Cure at 22C + 30 Minute Post Bake at 82C, Vs. Bond Conditions, Percent Fiber Tear, (%)**

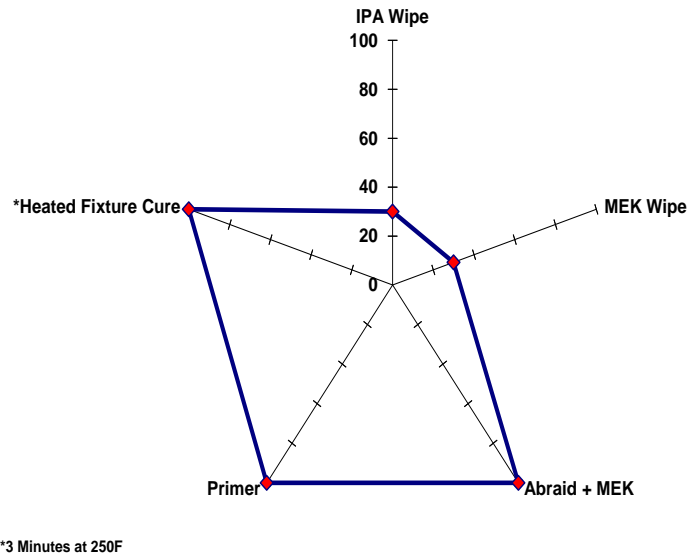


Figure 6: Radar Plot of Control Adhesive

## Data and Discussion

### Incumbent State of Urethane Adhesives

To illustrate the current state of technology as a baseline for this study a traditional two-part polyurethane adhesive was used to bond a standard SMC under a variety of common production conditions and tested at elevated temperature, 60°C, see Figure 6. The basic cure utilized represents the one most frequently requested for a room temperature cure application. Typically there is a period of time the bond is held in a fixture until green strength is obtained to hold dimensional tolerance. Depending on the size and weight of the part and how it's handled immediately out of the tool, green strength requirements may vary from 344 to 689 kPa. From this point the part is typically spray primed and baked at 82°C within three days. The work presented in the radar plot varies both surface preparation and cure conditions. The common cure cycle is 3 days at 22°C followed by 30 minutes at 82°C which represents a three day delay between bonding of the part and exposure to a paint bake. Surface preparation varies from solvent wipe, to surface sanding and primer application. Finally one point provides a typical heated fixture cure of three minutes at 121°C. This data clearly demonstrates the control adhesive requires either surface abrasion, primer application or a heated fixture cure to provide 100% fiber tear of the SMC at 60°C. As the process trend moves from a heated fixture cure to a room temperature cure followed by a delayed post bake it is clear additional surface preparation is required to generate successful adhesive bonding.

## A Market Solution

Recognizing a market need for better low temperature cure response, Ashland Inc. initiated a Design for Six Sigma<sup>\*1</sup> program to define performance targets and develop a product to meet this market demand. Several key molders and assemblers were consulted and several different composite types and formulations were identified as critical to customer success. From this list one formulation was selected representing each composite process, SMC, HSU and RTM to use as screening substrate for the development program. The room temperature cure followed by a low temperature post bake was retained as confirmed by the customer base. The goals for the program were laid out as follows:

- Fixture time < 25 minutes at 22°C
- Open time ≥ 5 minutes at 22°C
- Successfully bond SMC, HSU and RTM
- Pass Freightliner, Paccar and General Motors specifications
- Compatible with existing adhesive delivery systems
- Capable of being heat accelerated
- 1:1 ratio for ease of dispensing
- Non-flammable
- Acceptable odor
- EH&S acceptable

Extensive development work by the Global Technology Team at Ashland Inc. identified a new urethane system meeting these precise requirements. A new polymer created from allophanate modified isocyanate and a reactive non-ionic surfactant was shown effective when combined with a curative containing less than 5 equivalent percent total amino and hydroxyl groups having an equivalent weight greater than 500. The formula represents new technology and is currently patent pending. Figure 7 shows the results of the new combination over a radar plot as compared to the control. The data demonstrates satisfactory 60°C adhesion on SMC under all surface preparation conditions.

Obtaining positive results over one SMC at 60°C led to a broader investigation. Several different substrates were obtained from a number of well known composite molders and evaluated in lap shear vs. test temperature, from -30°C to 82°C, and immediately following a seven day water soak at 54°C. Figure 8 tabulates the results as percent passing failure pattern either fiber tear for the composites or cohesive for electro-coated steel. Using a three day ambient cure followed by 30 minutes at 82°C all samples yielded passing performance across the full temperature range. While this product is not expected to bond all composite formulas available it did perform well on this list of substrates.

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**60C Lap Shear Test Over SMC Following 72 Hour Room Temperature  
Cure at 22C\* + Delayed Post Bake 30 Minutes at 82C,  
Percent Fiber Tear, (%)**

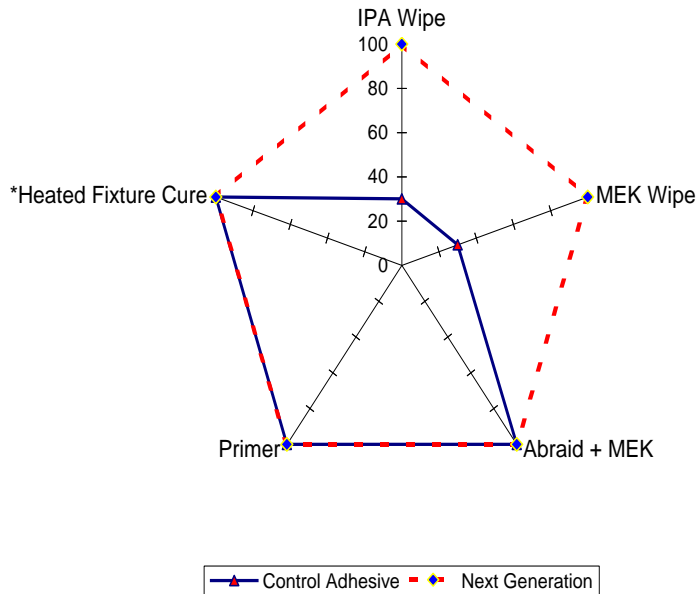


Figure7: New Technology Bond Performance

	22C	60C	82C	-30C	7 DWS
830R SMC	100	100	100	100	100
323IF SMC	100	100	100	100	100
9498-4 SMC	100	100	81	100	100
9496 SMC	100	96	100	100	100
269 SMC	100	100	100	100	100
310 SMC	100	100	100	na	100
2287 SMC	100	100	100	100	100
5449 SMC	100	100	100	100	100
In Mold Coating	100	100	100	100	100
E-Coat	100	100	100	100	100
HSU I	85	100	100	100	100
HSU II	100	100	na	100	100
RTM	100	100	na	100	100
Polyamide	100	100	100	na	100
RIM	100	100	na	100	100

Figure 8: Does it Stick, (% FT)

The next set of experiments sought to optimize the open time at five minutes and then determine the time to build strength to both 344 and 689 kPa, (50 and 100 psi respectively). These are key adhesive parameters since the open time represents the time within the parts need to be mated and the strength available to hold dimensional stability the moment the fixture opens. Figure 9 shows the results of cross peel strength testing at 22°C. Using an average of three samples, the open time was measured to be about 5 minutes and the system yielded 344 kPa in about 20 minutes and 648 kPa in about 25 minutes. The ratio of strength build time to open time is approximately 4 to reach 344 kPa and 5 to reach 689 kPa.

Often assembly processes require either longer or shorter open times to allow time to apply a longer bead of adhesive, assemble more complex geometries or account for changes in ambient temperature. To demonstrate capability the basic curative was modified slightly to create variable open times from 4 to 30 minutes with results shown in Figure 10. The plot also demonstrates the associated time to reach a minimum green strength of 344 kPa in the cross peel configuration at 22°C. As the reaction is slowed through curative modification, it manifests as both a longer open time and time to reach green strength. While only the five minute open time product is commercially available it does demonstrate potential to adjust the cure parameters to meet demanding process scenarios.

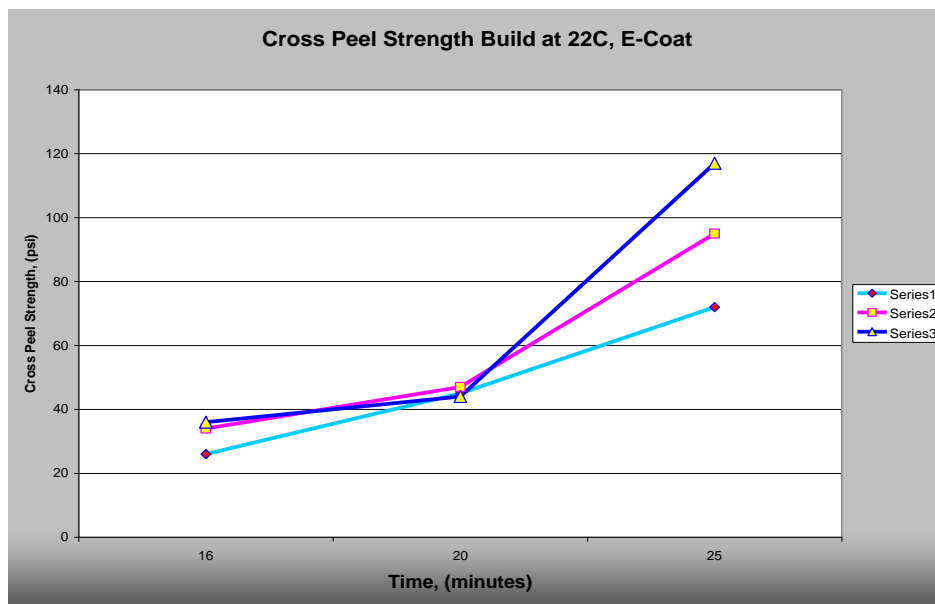


Figure 9: Strength Build at 22°C

The next series of experiments sought to determine the minimum post bake temperature required to achieve fiber tear performance at elevated temperature, 60°C, following the room temperature cure. Figure 11 demonstrates data for both RTM and SMC while Figure 12 reviews the performance over HSU. Starting at 104°C the post bake temperature was incrementally reduced to a minimum of ambient temperature or no post bake. Lap shear coupons from each exposure were evaluated at 60°C and plotted as percent fiber tear. Figure 11 exhibits uniform 100 percent fiber tear patterns through the full spectrum of post bake temperatures. Thus demonstrating over the selected SMC and RTM it is not necessary to provide a post bake to achieve 100% fiber tear at 60°C. A similar series was performed on HSU samples with slightly different results. Figure 12 follows the same post bake pattern used in Figure 11 but illustrates the requirement for a post bake of at least 82°C to obtain fiber tear at 60°C over HSU.

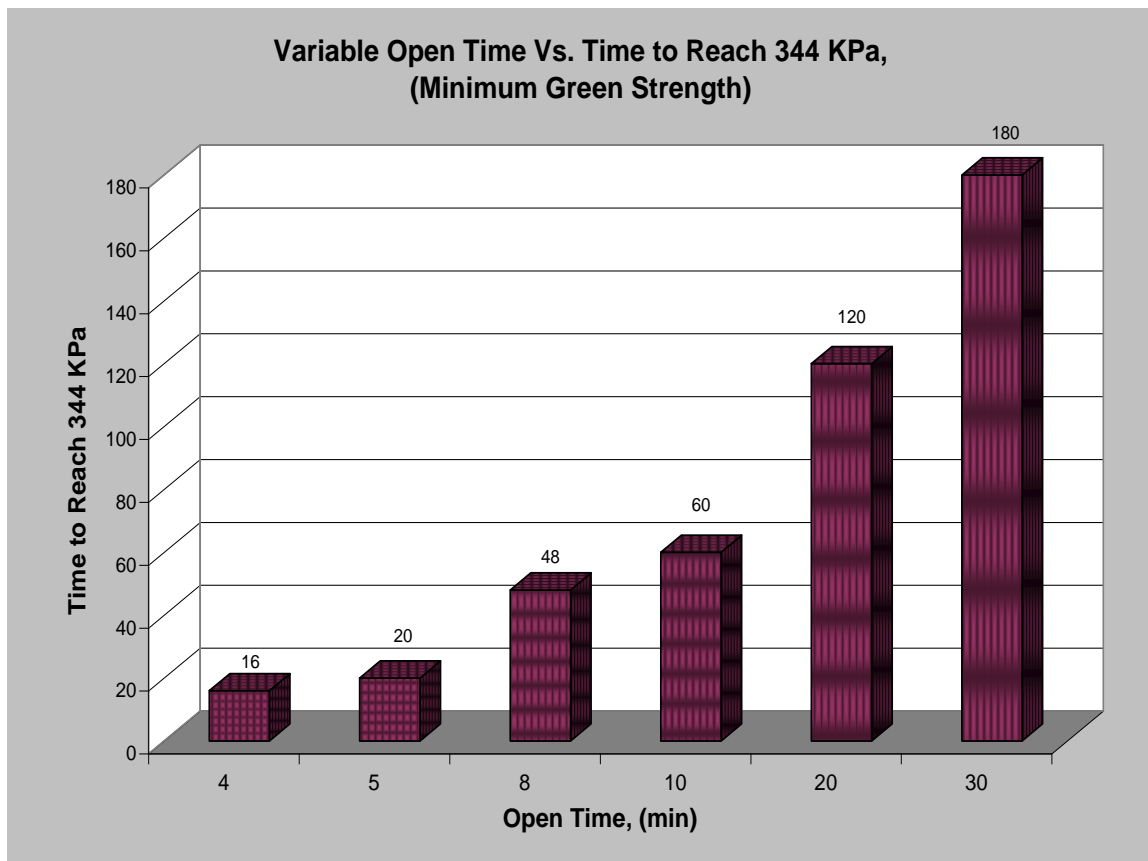


Figure 10: Open Time vs. Time to Green Strength

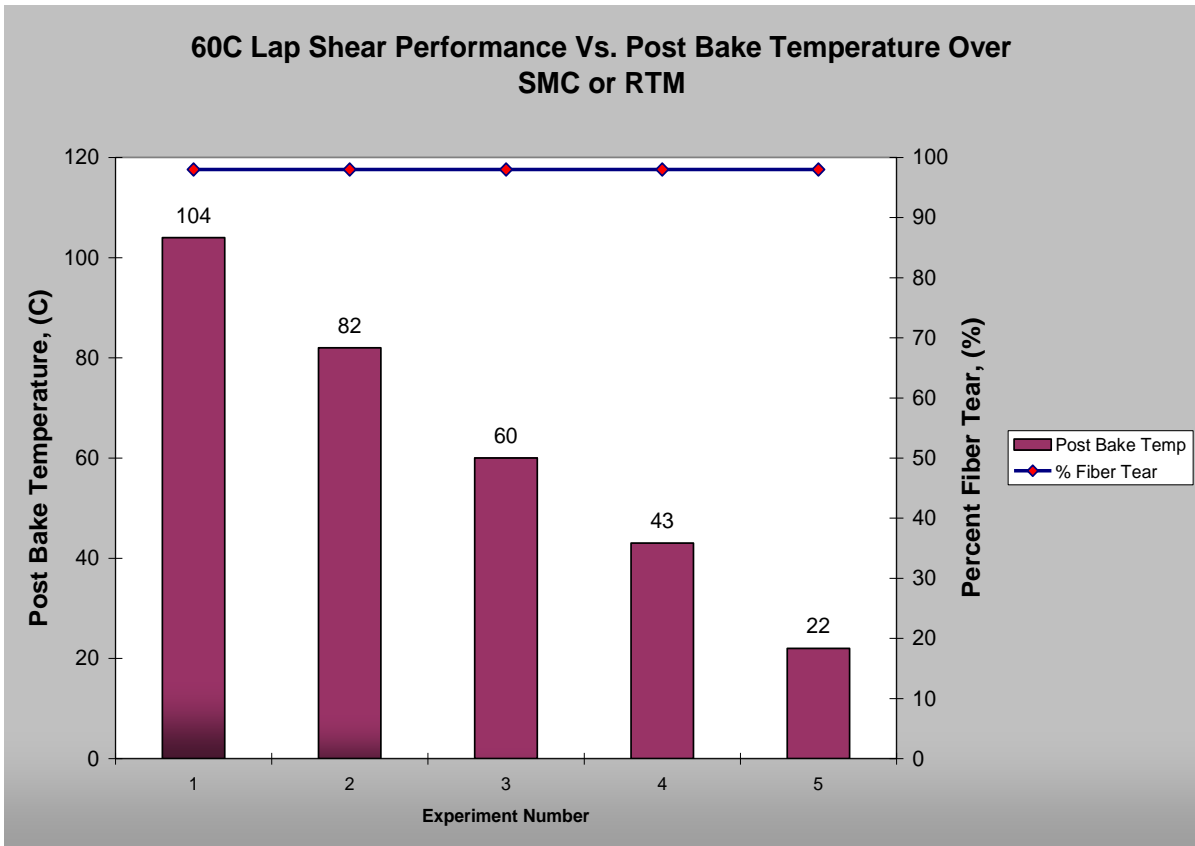


Figure 11: Post Bake Requirements Over SMC or RTM

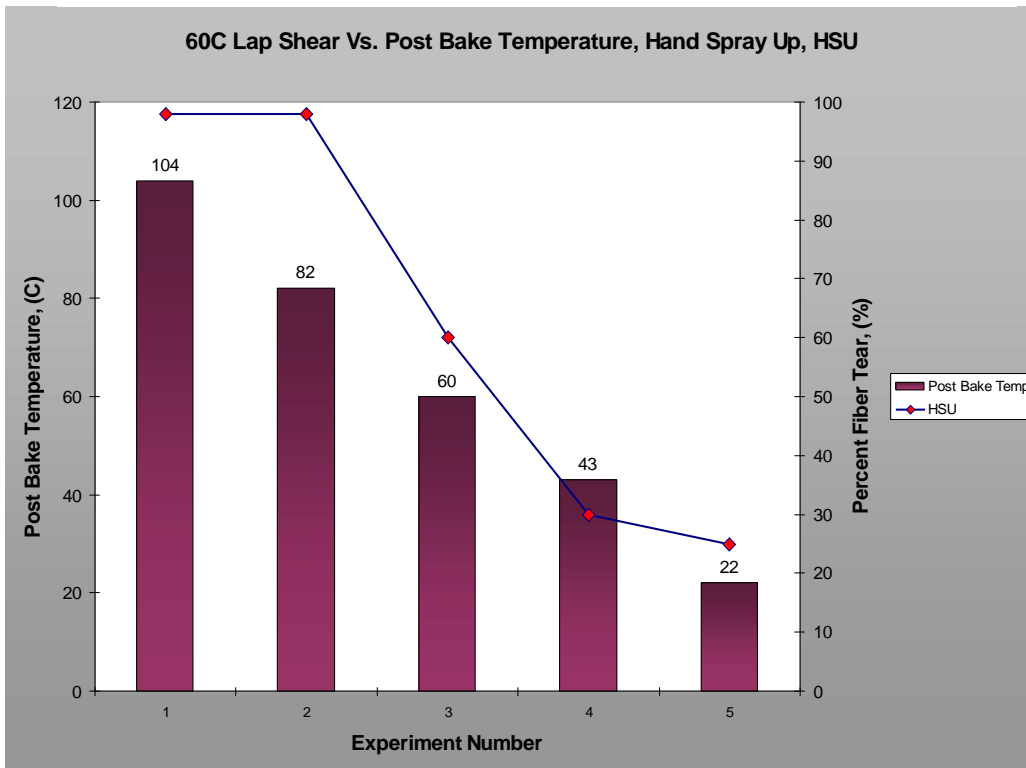


Figure 12: Post Bake Requirements Over HSU

Further characterization was performed by generating bulk mechanical properties of the new system and the data are shown vs. a standard heat cure polyurethane system in Figure 13. The new technology was cured for 72 hours at 22°C and the control was baked for 33 minutes at 149°C. Tensile strength is a measure of the bulk strength of the product and is the maximum strength the adhesive may achieve in a bond test under ideal conditions. The new technology registers over 58% stronger than the heat cured control. Young's modulus is a measure of the relative stiffness of the polymer and the new technology is more than four times higher relative to the heat cured system without the requirement of a post bake. The stiffer product would be expected to yield lower elongation and indeed was observed, 38% vs. 54% for the heat cured system. However, only 16% elongation was sacrificed to obtain a 440% increase in modulus and 58% improvement in strength while maintaining robust adhesion. The glass transition temperature of the RT cure system is 12°C less than the heat cured product but will continue to advance during a 82°C post bake to 72°C reducing the differential to just 3°C.

	New Technology	Control, Heat Cured
Tensile Strength, MPa	25.4	16
Young's Modulus, MPa	1590	364
Elongation, %	38	54
Poisson Ratio	0.39	0.52
Glass Transition °C	62	75
Tg Post 82C Post Bake	72	na

Figure 13: Bulk Mechanical Properties

While not the design intent of this technology, it may on occasion be necessary to heat accelerate the cure of the adhesive to meet a faster process requirement. Figure 14 demonstrates the affect of varying temperature on the time to build green strength in cross peel when tested at the stated cure temperature. With heat at 100°C the time to 344 kPa green strength is reduced to five minutes and to reach 689 KPa 11 minutes. These times are reduced to less than two minutes by raising the temperature to 121°C.

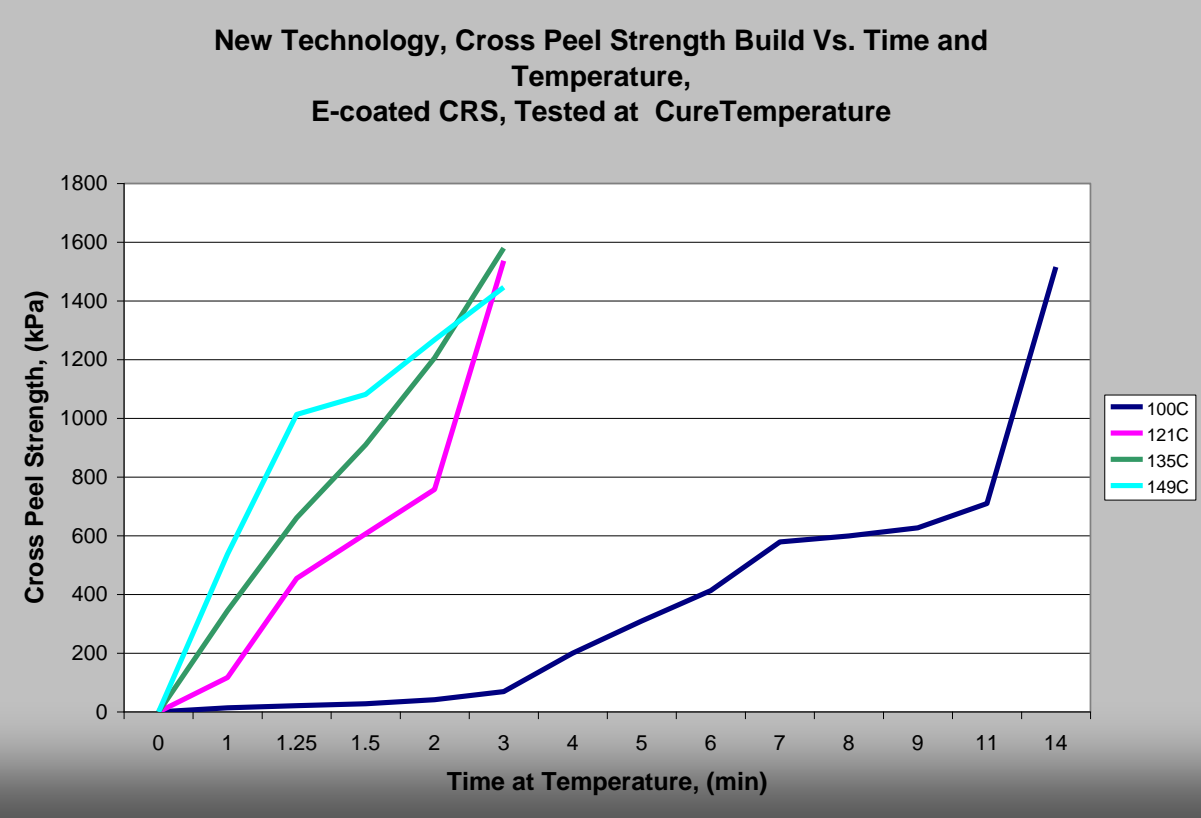


Figure 14: Cross Peel vs. Time and Temperature

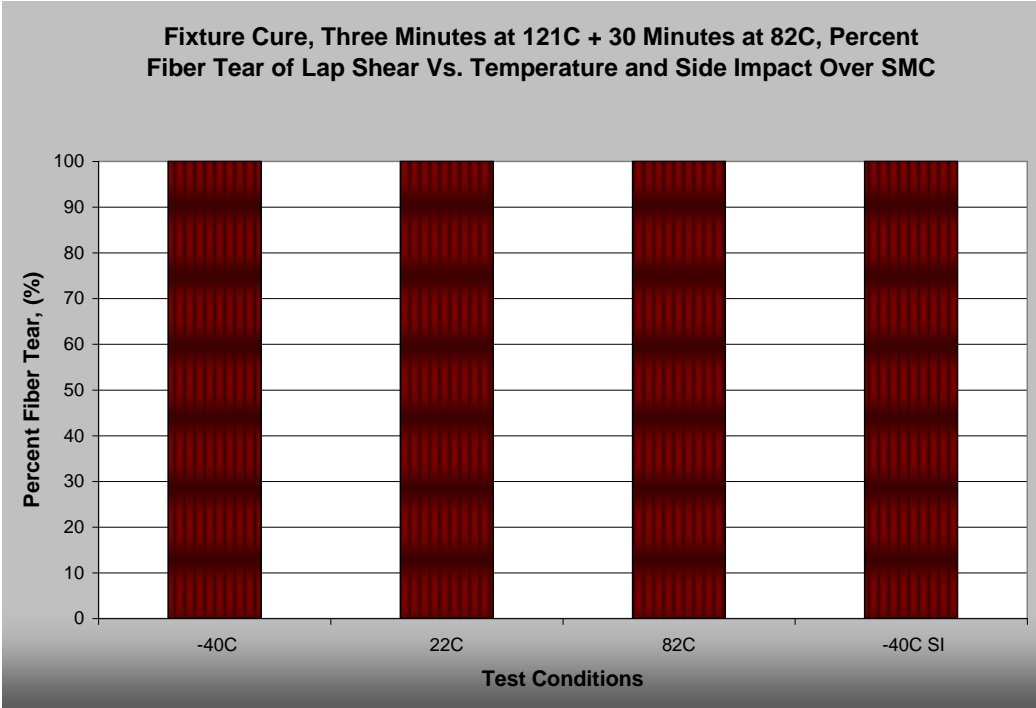


Figure 15: Fixture Cure Bond Performance

To determine if fixture heat curing has a negative affect on the adhesive, a short series of bonds were generated on SMC substrates. Figure 15 plots the results as percent fiber tear vs. test type. Both lap shear vs. temperature and sub-ambient side impact, SI, were evaluated all with 100% fiber tear. While to date there have not been full specifications completed following a fixture cure process, the data are positive and supports additional testing which is underway in our laboratory.

Primary composite molders in the transportation industry generally require successful completion of OEM engineering specifications to qualify an adhesive for use. These specifications typically expose bonded samples to a variety of temperature and cyclic environmental exposures to ensure in-service survivability. Three primary standards were evaluated with the improved technology using a 72 hour cure at 22°C followed by 30 minutes at 82°C. Figure 16 tabulates the specifications and the substrates evaluated. The PACCAR<sup>\*2</sup> specification is considered difficult to pass due to its severe cyclic durability exposures ranging from hot, cold, water soak, humidity and salt spray, therefore, all three substrates, RTM, HSU and SMC were evaluated. General Motors and Freightliner specifications were also evaluated but only with bonded SMC. All three specifications were successfully passed demonstrating 100% fiber tear in all substrates and tests evaluated.



Figure 16: Successfully Completed Specifications

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<sup>2</sup> “Third Party Registered Trademark”

## **Summary and Conclusions**

This paper has drawn attention to the lack of room temperature cured performance at elevated temperature using current two-part polyurethane technology when bonding composite substrates. It also announces the development of a new prepolymer based on allophanate modified isocyanate and modified curative designed to fill this performance gap. Data was presented to demonstrate the robust adhesion of the new product to SMC, RTM and HSU and its ability to vary open times. Strength build was shown to vary from 4 to 6 times the open time to reach minimum green strength. While the primary cure cycle included both a room temperature cure at 22°C and a post bake at 82°C it was demonstrated over selected SMC and RTM that the post bake was not required to achieve fiber tear failure patterns. Bulk mechanical property determination revealed an improvement of 440% in modulus and 58% improvement in tensile strength while maintaining good elongation. Several primary engineering specifications were completed with positive results over SMC, RTM and HSU. This package clearly supports the successful development of a new class of two-part polyurethane adhesive for use in bonding composite.

## **Acknowledgements**

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