# Advances In Benzoxazine Resins For Aerospace Applications

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## ABSTRACT

Benzoxazine resins offer high temperature performance, low moisture uptake, good flame, smoke and toxicity, and the potential for ambient storage. This paper describes the development of benzoxazine resins for aerospace applications focusing on liquid resin technologies, including resin transfer molding (RTM) and vacuum assisted RTM (VARTM). For these applications ease of processing is required and resins have been formulated with suitable viscosity and the thermal stability at process temperatures. A compatible binder has been developed which allows fabric preforming, does not affect the temperature performance, and provides composite toughness similar to that of toughened prepreg systems.

A further step is the development of a benzoxazine resin which has high intrinsic toughness without the use of a binder, and can be processed by RTM/VARTM techniques. This opens up the possibility of high temperature performance and high toughness in 3-D weaves and preforms where it is impractical to insert a binder or veil.

## 1. INTRODUCTION

The aerospace industry is constantly striving to improve performance and reduce cost of the structures. Many advances have been made in materials performance, design and manufacturing for recent aerospace programs [1]. One of the technologies that have proved to be particularly successful is liquid resin processing, in which the resin is infused into a fiber perform during manufacture of the finished article. This class of processes includes resin transfer molding (RTM), vacuum assisted RTM (VARTM) and resin film infusion (RFI) [2]. These techniques have enabled significant cost reductions through single-step manufacture of the finished structure, integration of different elements (e.g. skin and stiffeners), and elimination of fasteners.

In addition, there are design benefits through the ability to put fibers in the required orientations and to mitigate out of plane loads through the use of through thickness reinforcement. These advantages have led to applications on current aircraft programs [2]. Resins with the required characteristics are needed in order to make effective use of these technologies. The resins must meet aerospace requirements such as temperature performance, mechanical properties, toughness, fluid resistance etc. The resins must also have the required processing characteristics, for example viscosity profile, minimum viscosity and gel point to enable impregnation of the reinforcement. This creates many challenges for the resin formulator.

The resin characteristics which are required for high toughness generally result in high viscosity of the resin. This has led designers to make many trade-offs in selecting resin systems. Materials developers have found creative ways to mitigate these challenges by the use of second phase toughening in the form of powders, fibers or veils, in order to retain the processing characteristics required for liquid resin processing [2, 3] Benzoxazine resins have recently created significant interest as matrices for composite applications [4, 5]. Henkel has presented previous work on our development of Epsilon™ benzoxazine resins [6, 7]. The formulations offer the potential for:

- high service temperature,
- low moisture absorption,
- room temperature stability,
- low cure exotherm,
- low resin shrinkage on cure, and
- good flame, smoke and toxicity performance

Epsilon benzoxazine resins have been formulated for use in liquid resin processing application. The initial evaluations of benzoxazine liquid resins have been described previously [6]. This work describes the evaluation of further developments of Epsilon benzoxazine liquid resins.

## 2. EXPERIMENTAL

### 2.1 Materials

Two resin systems and a compatible binder system were evaluated:

- Epsilon 99110 is a high temperature performance benzoxazine resin system designed for a broad range of applications.
- Epsilon 99120 is a toughened benzoxazine resin.
- Epsilon 99900 is a binder which is compatible with the Epsilon resins.

The binder fulfills two functions: it can be used for preforming and compaction of the reinforcements, and it provides additional toughening. The binder was applied to the reinforcements and compacted at 120 °C for 30 minutes under vacuum. Resin castings were cured at 180 °C for 90 minutes with a pressure of 621 kPa. The resins were infused into a variety of reinforcements using either RTM or VARTM processes.

RTM processing was performed using a Radius Engineering pneumatic injector with an injection pressure of 240 kPa into matched metal tools. Pressure was increased to 690 kPa and the tool was heated up at a rate of 0.5-2 °C/minute to 150 °C. The temperature was held at 150 °C for 30-120 minutes depending on the size and geometry of the laminate. The laminate was further heated at 0.5 – 2.0 °C/minute to 180 °C, and cured at 180 °C for 90 minutes.

VARTM processing was performed using a double bag technique. Vacuum of 90% of atmospheric pressure was used for infusion. After infusion the inlet and outlet of the inner bag were closed and full vacuum applied to the outer bag. The laminate was heated up at a rate of 0.5-2 °C/minute and cured at 180 °C for 90 minutes.

The quality of the resulting laminates was confirmed by visual inspection, cured ply thickness and ultrasonic C-scan.

### 2.2 Testing

Rheology of the resins systems was evaluated in several ways. Temperature sweeps were performed using TA Instruments RDA II rheometer using a cup and plate configuration, with a heat-up rate of 2 °C/min, frequency 10 rad/sec, and a maximum strain of 10%. Isothermal viscosity was measured using a TA Instruments AR2000 rheometer using cup and plate with a frequency 10 rad/sec and a maximum strain 30%.
Mechanical and flammability testing were performed on cured resin and composite samples using standard test methods as described in the results.

## 3. RHEOLOGY

### 3.1 Temperature Characteristics

Temperature sweeps for the two resins are shown in Figure 1. For successful resin infusion the viscosity needs to be below 10 Poise, and ideally below 5 Poise [8]. Based on this range we have used a viscosity of 7 Poise as the upper limit for infusion. From Figure 1 it can be seen that the temperature at which the viscosity drops below 7 Poise is 78 °C for Epsilon 99110, and 93 °C for Epsilon 99120. If the resin viscosity becomes too low then resin will ‘racetrack’ in the tool, flowing around the preform which, can create areas which do not have complete impregnation.

The minimum viscosity which is preferred in order to avoid this is approximately 0.5 Poise. The minimum viscosity of Epsilon 99110 is 0.6 Poise and of 99120 is 1 Poise, therefore both resins may be processed over the full temperature ranges. It can also be seen that the change in viscosity with temperature is relatively small for both resins over the temperature range 100-120 °C. From this initial assessment an infusion temperature of 110 °C was chosen for further evaluations.

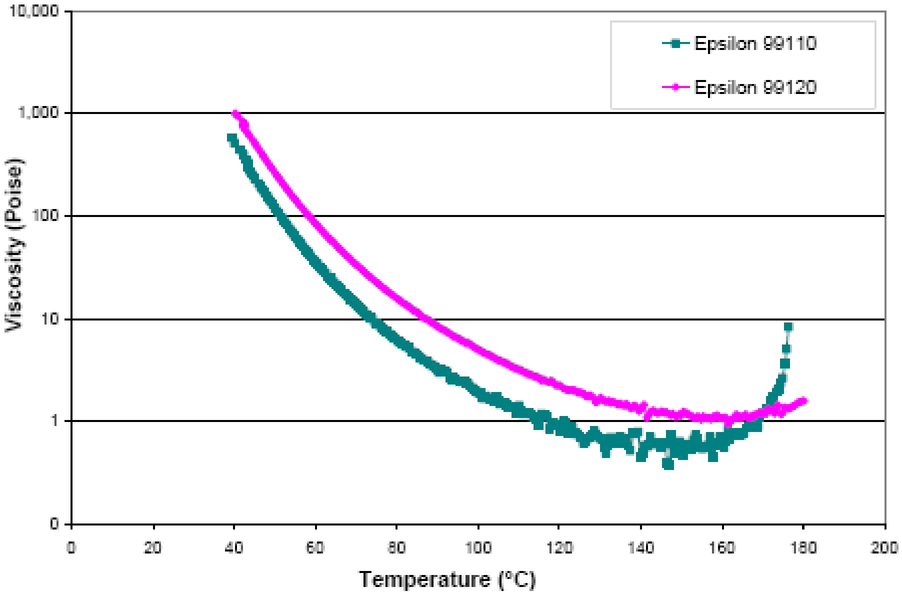


*Figure 1. Viscosity-Temperature sweeps for Epsilon 99110 and Epsilon 99120*

### 3.2 Isothermal Viscosity

The next aspect of processing is the time at which viscosity remains in the process range, i.e. below 7 Poise, at the infusion temperature. This will determine the maximum infusion time and therefore gating for the mold, and the maximum size of the parts which can be manufactured. In general a higher process temperature will give lower initial viscosity, but the viscosity will increase more rapidly due to resin reactivity. The isothermal viscosity for the two resins at 110 °C is shown in Figure 2. The viscosity of both resins increases slightly over time, and the viscosity of both resins is below 3 Poise after 2-hours at 110 °C. This demonstrates the process stability of the resins. Therefore both resins have a broad process window in terms of infusion temperatures and times.

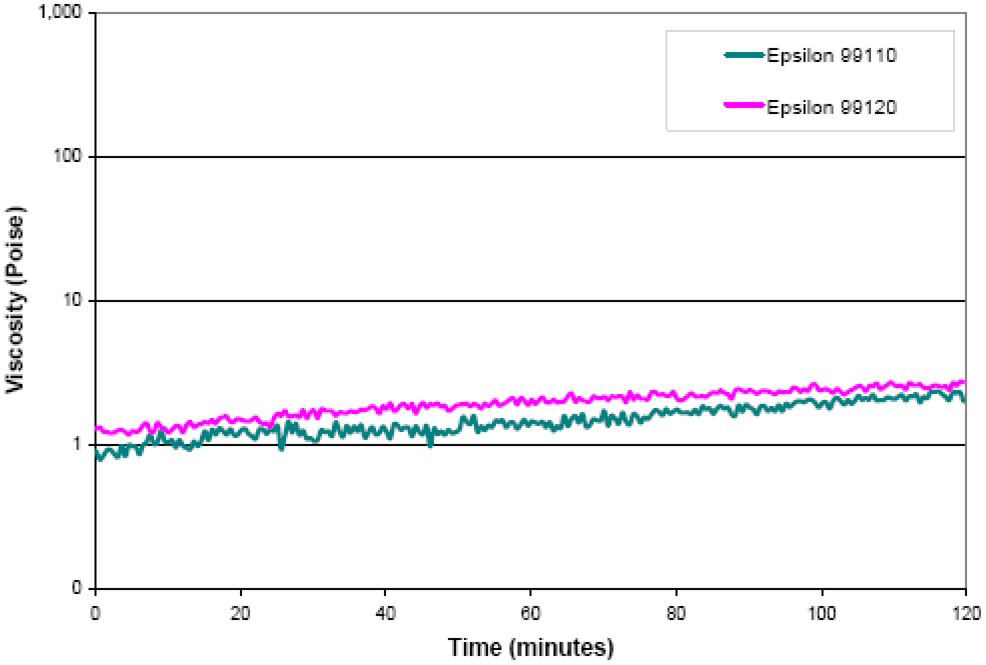


*Figure 2. Isothermal viscosity of Epsilon 99110 and 99120 at 110 °C*

## 3.3 Ambient Temperature Storage

Benzoxazine resins have the potential for extended storage at ambient temperature without detriment to their processing characteristics. The combined effects of storage time and isothermal processing time for Epsilon 99110 are shown in Figure 3. After 6-months storage at room temperature and 2-hours at 110 °C the resin still has acceptable infusion characteristics. This opens up a much wider range of shipping, storage and processing windows than are possible with current epoxy and bismaleimide resins.

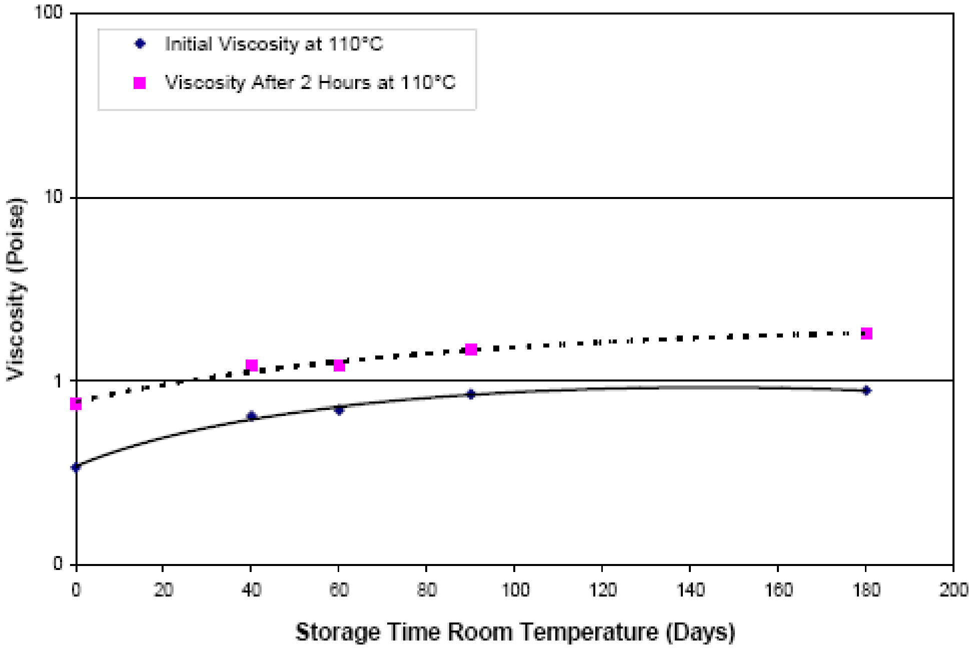


*Figure 3. Isothermal viscosity of Epsilon 99110 at 110 °C after storage at 23 °C for 6-months*

## 4. CURED RESIN PROPERTIES

### 4.1 Resin Physical Properties

The physical properties of the cured resins are shown in Table 1. Both resins have high degrees of cure, greater than 90%, and similar densities. Glass-rubber transition temperature (Tg) was determined from the extrapolated onset of storage modulus drop. Both resins have Tgs which meet aerospace service temperature requirements. Composite Materials Handbook-17 [9] guidelines for epoxy resin composites are that the maximum service temperature should be no more than 28 °C below the wet Tg. Using this criterion the service temperatures for the two resins are:

Epsilon 99100: 133 °C
Epsilon 99120: 119 °C

*Table 1. Cured Resin Physical Properties*

| Property | Epsilon 99110 | Epsilon 99120 |
|---|---|---|
| Cure percentage, % | 93 | 98 |
| Density, $\text{g/cm}^3$ | 1.22 | 1.21 |
| Tg, DMTA, ASTM E1640, °C | | |
| Dry | 191 | 180 |
| Wet[1] | 161 | 147 |
| Weight change on moisture conditioning[1] | 2.6 | 2.9 |

1. 72-hours in boiling water

### 4.2 Resin Mechanical Properties

Mechanical properties of the cured resins are shown in Table 2. Both resins have the strength and modulus required for high performance composite performance. Epsilon 99110 is optimized for stiffness, while Epsilon 99120 is optimized for toughness, and this is seen in the higher elongation and fracture toughness of this resin.

*Table 2. Cured Resin Mechanical Properties*

| Property | Epsilon 99110 | Epsilon 99120 |
|---|---|---|
| Flexural strength, ASTM D790, MPa | 160 | 148 |
| Flexural modulus, ASTM D790, GPa | 4.5 | 3.5 |
| Tensile strength, ASTM D638, MPa | 97 | 106 |
| Tensile elongation at failure ASTM D638, % | 1.5 | 4.6 |
| Tensile modulus, ASTM D638, GPa | 3.7 | 3.5 |
| Fracture toughness, ASTM D5045, $\text{J/m}^2$ | 112 | 512 |

## 5. COMPOSITE PROPERTIES

### 5.1 Composite Mechanical Properties

Mechanical properties of Epsilon 99110/carbon fabric composite at room temperature are shown in Table 3. The reinforcement is a 5-harness satin weave with standard modulus carbon fiber. The results show good translation of fiber dominated properties in tension, and high compression strength, confirming the effect of the high resin modulus. The shear properties are comparable to those of current epoxy matrix composites.

*Table 3. Epsilon 99110/5-Harness Carbon Fabric Mechanical Properties*

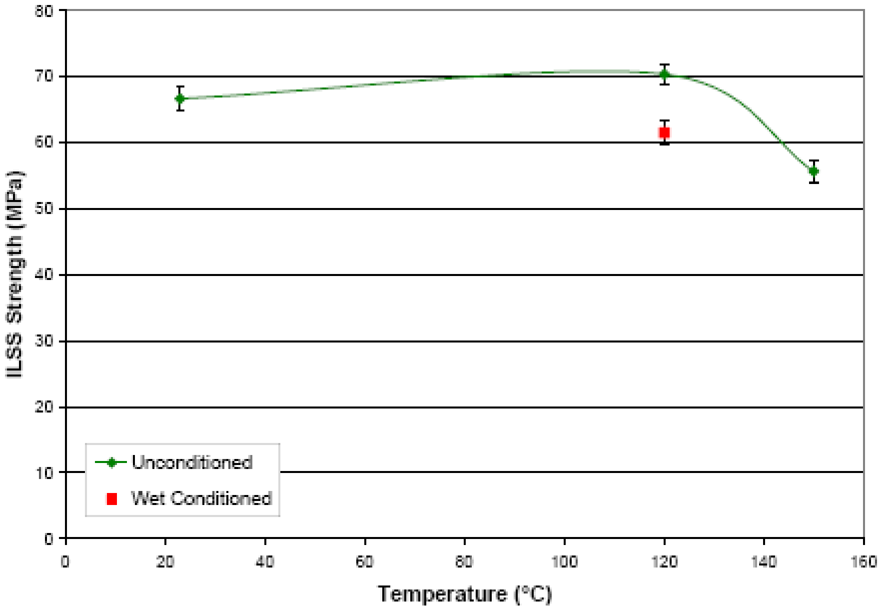
| **Property** | **Lay-up** | **Test Direction** | **Modulus** | **Strength** |
|---|---|---|---|---|
| Tension | $[(0/90)]_6$ | 0° | 72.1 | 1,028 |
| | | 90° | 71.8 | 973 |
| Compression | $[(0/90)]_6$ | 0° | 63.7 | 934 |
| | | 90° | 68.3 | 1,009 |
| In-Plane Shear | $[(\pm45)]_6$ | 0° | 5.91 | 99.0 |
| Interlaminar Shear | $[(0/90)]_6$ | 0° | - | 66.7 |

Carbon fiber, standard modulus, 6k
5-Harness satin weave 370g/$m^2$ with Epsilon 99900 at 10% coating weight
RTM processed
Results normalized to 60% fiber volume fraction

## 5.2 Effect of Temperature on Composite Properties

The effect of temperature on a resin dominated property of Epsilon 99110 composites was assessed using interlaminar shear strength (ILSS). Strength was tested on unconditioned specimens at room temperature, 120 °C and 150 °C. In addition specimens were tested at 120 °C, after conditioning at 70 °C and 85% relative humidity environment to equilibrium weight change. The material shows no loss in ILSS at 120 °C unconditioned and 92% retention after moisture conditioning. The ILSS retention at 150 °C unconditioned is 83%. These test results confirm that the service temperature of Epsilon 99110 composites meets or exceed the value of 119 °C expected from the Composite Materials Handbook-17 formula. Indeed the 28 °C delta between wet Tg and maximum service temperature used for epoxy resins may be too conservative for the benzoxazine chemistry.

*Figure 4. Effect of temperature on Interlaminar Shear Strength for Epsilon 99100 / 5-harness satin fabric, standard modulus carbon*



### 5.3 Composite Toughness Properties

Compression after impact (CAI) strength was used to assess the damage tolerance capabilities of the material. Specimens 150 mm x 100 mm were tested with an impact energy of 30 J. The CAI strength of toughened epoxy prepreg systems is in the range 240-273 MPa [10, 11]. The results on Epsilon 99110 show the benefits of the Epsilon 99900 binder, with CAI strength increasing from 201 MPa without binder to 276 MPa with binder. There is also an increase for Epsilon 99120 but the improvement is not as great because of the higher intrinsic toughness of this resin. Even without the binder the CAI strength of Epsilon 99120 is in the same range as state of the art prepreg systems. This opens the opportunity to manufacture complex parts, using liquid resins and three-dimensional performs without the need for additional toughening agents.

*Table 4. Compression After Impact Strength*

| **Resin** | **No Binder** | **10% Binder** |
|---|---|---|
| Epsilon 99110 | 201 MPa | 276 MPa |
| Epsilon 99120 | 241 MPa | 290 MPa |

Standard modulus 3k carbon fiber
Plain weave 193 $g/m^2$ with Epsilon 99900 at 10% coating weight
24-ply quasi-isotropic lay-up $[(\pm45)(0/90)]_{6S}$
VARTM Processed
Test Method AITM1-0010

### 5.4 Composite Flammability Properties

Flame, smoke and toxicity (FST) testing was performed on Epsilon 99110 laminates manufactured using RTM processing. The reinforcement was the 5-harness satin fabric with 10% Epsilon 99900 binder as used previously. The laminates were evaluated in the ‘flaming mode’ since this represents the most demanding case. The results are summarized in Table 5 along with the standard requirements for these tests. The smoke density is less than 30% of the maximum requirement and the toxic gasses released are well below acceptable ranges.

*Table 5. Smoke and Toxicity Properties of Epsilon 99110/Carbon fiber composites*

| **Property** | **Maximum Allowable** | **Epsilon 99110/UD(1)** |
|---|---|---|
| Lay-up | | [(-+45)(+-45)]s |
| Laminate thickness | | 1.7mm |
| Smoke Density Ds after 4minutes<br>Flaming Mode<br>FAR Part 25 Appendix F, Part V | 200 | 58 |
| Toxic Gas<br>Gas sampling taken after 4minutes<br>Flaming Mode<br>Test Method ABD0031 | | |
| HCN | 150ppm | 1ppm |
| CO | 1,000ppm | 90ppm |
| $NO_X$ | 100ppm | 10ppm |
| $SO_2 + H_2S$ | 100ppm | 0ppm |
| HF | 100ppm | 0ppm |
| HCl | 150ppm | 0ppm |

Carbon fiber, standard modulus, 12k
5-Harness satin weave 370$g/m^2$ with Epsilon 99900 at 10% coating weight
RTM processed

## 6. CONCLUSIONS

Henkel has developed benzoxazine resins to compliment existing epoxy and bismaleimide resin systems for liquid resin processing. The benzoxazine resins offer easy processability for RTM and VARTM processing, long storage time at ambient temperature and extended infusion time at process temperature. The composites manufactured with the resins meet or exceed aerospace mechanical performance criteria, and service temperature requirements. In particular the resins provide the same level of damage tolerance as achieved with state of the art toughened epoxy resins. In addition the flammability resistance of the resins enables the composites to easily meet industry requirements. The evaluations here confirm that the Epsilon benzoxazine resins offer a combination of processing and performance to meet aerospace requirements, and they expand the portfolio of available resins for the growing area of liquid resin processing.

## 7. REFERENCES

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