

# Henkel Technologies and Products for China Aerospace

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**Abstract:** Epoxy structural adhesives and composites have been in use for many years for the construction of aerospace vehicles. Henkel provides many epoxy products. Many other resin systems have been evaluated and several, such as imide, phenolic and cyanate ester, have also achieved significant use. Henkel's newly developed "Epsilon" chemistry demonstrates unique features that benefit application in aerospace structure that use adhesives and composites.

**Key words:** adhesive; composite; epsilon; matrix resin; structure

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Epoxy structural adhesives play a critical part in the fabrication of aerospace structures. Epoxies have been used for their strength and durability and their resistance to the effects of fluids and water. Substrates have advanced over the last 20 years from metals, primarily aluminum on flight structures such as rudders, elevators, ailerons and nacelles to composites on many of these components. Composites have advanced from glass fiber to Kevlar and to graphite composites. Graphite composites have increased in strength and toughness and have now advanced from wing components to the fuselage and the wing. All along the way, epoxy adhesives have played that critical role allowing design changes to be advanced. More recently other chemistries have also contributed because of unique properties. Epsilon chemistry shows excellent potential for future commercial use in building aerospace structures.

In the world of aerospace structure, the two predominate forms of aerospace part construction are honeycomb-stiffened structure and rib-stiffened structure. With the advent of large scale composites and the related processes of automated tape laying, resin transfer molding and resin film infusion, we are also seeing the advancement of net shape molded parts where the product uses less secondary bonding. We also see that these automated and advanced processes mark a move away from hand lay-up prepreg assembly and more into dry fiber/preform construction impregnated with resin during structural part fabrication.

tion.

## 1 Epoxy Systems

### 1.1 Honeycomb and Rib Stiffened Structure

Honeycomb and rib stiffened structure use primarily film adhesives for structural bonding. Metal honeycomb bonding with aluminum substrates desires film adhesives with high degrees of toughness or peel. While the peel properties are not used for design purposes, *i.e.* they are often less than 445N/25 mm in strength; this feature provides durability to match the characteristics of metal. Metals bend and absorb some of the flexural load and the adhesive needs to be durable during this bending. Plus, metal parts are usually subject to secondary drilling and machining processes and the adhesive must have enough toughness to withstand these fracture type forces.

The most common adhesive from this family of products is Hysol EA 9696 shown in Fig. 1. It is used primarily on metal-to-metal and metal-to-honeycomb bonding. It is qualified to Boeing's metal bonding specification BMS 5-101 and also to Boeing's 121 °C composite bonding specification BMS 5-129. It features 13.8 MPa at 121 °C tensile lap shear strength and has honeycomb climbing drum peel of 110N/25 mm. It also has excellent resistance to moisture and good flow properties. Adhesive flow is usually higher in metal bonding adhesives because the adhesive has to adequately wet-out the phosphoric or chromic acid-

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anodized surfaces of metal. Typically, metal surfaces and honeycomb core use a chromated solvent or water-based primer to seal the anodized surface. Slightly higher film adhesive flow aids in the wet-out of metal surfaces.

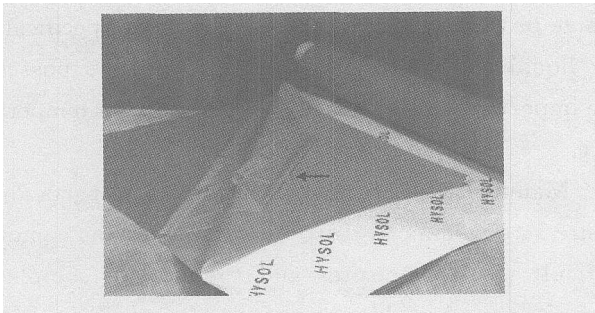


Fig. 1 EA 9696 film adhesive

The use of honeycomb stiffened structures requires joining various pieces of core, sometimes of different density, to allow one continuous load path through the structure. Foaming adhesives that expand upon cure, commonly called core splices, are used for this application. These film adhesives contain blowing agents or expanding fillers that allow the material to readily fill the gap between two pieces of core as shown in Fig. 2. Henkel's product for this application is Hysol MA 562 and is used throughout the world for core splicing applications.

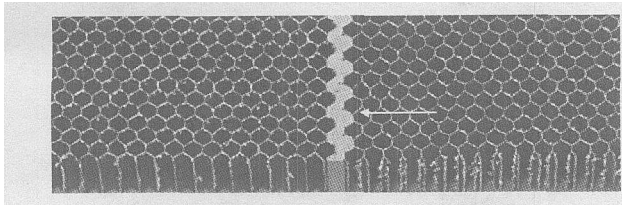


Fig. 2 Core splice

For more structural applications, Henkel supplies a closed cell expanding epoxy film called SynSpand 9899CF. SynSpand 9899CF can be used to fill honeycomb core for high strength attachments on load points. See Fig. 3.

High viscosity glass microballoon filled paste adhesives are commonly called syntactic pastes and are used to fill honeycomb core (potting) where fasteners or extra rigidity is needed. One common product in this family is Hysol EA 9396. 6MD. Hysol EA 9396. 6MD has compressive strengths of approximately 26.2 MPa and a room temperature cure with

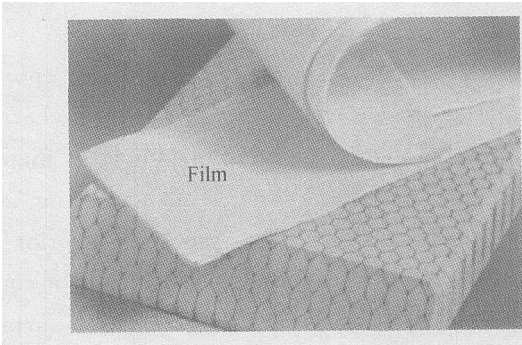


Fig. 3 Film and filled core

high temperature performance. For aerodynamic filling and fairing, Hysol EA 960F is typically used. It features a fast cure time with easily sandable surfaces.

1.2 Composite Structure

Composite bonding applications prefer a lower flow and a slightly lower toughness than metal bonding applications. This is because the modulus of composites is higher and the design of composites does not have to take into account the bending seen in metal substrates. Lower flow minimizes intermingling of prepreg resins. Most composites that are bonded use peel ply either dry or wet to provide a rougher surface to enhance mechanical bonding. Hysol EA 9695 is our leading composite bonding film used at Airbus for the A380 and newer applications and Hysol PL 7000 is our leading composite bonding film for Boeing BMS 5-154 applications. Both of these products have the ability to cure at either 121 °C or 177 °C. And both have the ability to operate at service levels of 177 °C. Designers typically construct around hot/wet  $T_g$  because it is more indicative of in-service environments. Wet  $T_g$  are about 25 ~ 50 °C lower than dry  $T_g$  and are dependent on the amount of absorbed water.

Composites also lend themselves to more unique and cost/weight-saving designs. One way to reduce the weight of composite structures is to use syntactic (glass microsphere filled) thick epoxy films. SynCore 9872. 1 and SynCore 9823. 1 can be used to substitute for additional graphite plies to achieve desired rigidity in a solid laminate structure. These materials are about a third lighter than solid graphite and have the ability to be used as edge close-outs or in the center of graphite parts.

Composite parts also require additional epoxy-based materials to allow it to match up with characteristics found in metal. As mentioned before, metals require a surface treatment such as anodizing and priming to prepare and protect the surface prior to bonding. Similar to enhancing the surface of a composite, one must either abrade and clean the surface or preferably use a peel ply. The peel ply serves as a removable layer that imparts a desired surface roughness for secondary bonding. Henkel provides Hysol EA 9895 which provides an optimum surface with easy removal and minimization/ elimination of any contaminating transfer. See Fig. 4 below.

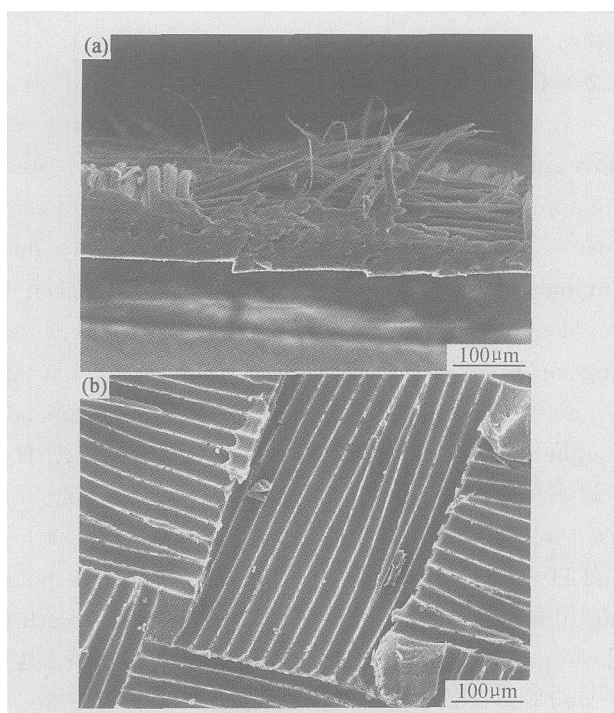


Fig. 4 Top shows fiber contamination,  
bottom shows only resin

The top picture is the surface of a cured composite after removal of the peel. It shows a lot of peel ply fiber remaining as contaminant. The bottom picture is the surface of a cured composite after removal of EA 9895 peel ply. It shows no fiber remaining.

Additionally, composites can not be machined to the tight tolerances of metal parts. Fit-up problems between skins and rib stiffeners can be resolved by using liquid shims, which are high-filled paste adhesives. Henkel's Hysol EA 9394 and Hysol EA 9377 are two of the most commonly used liquid shims. Hysol EA 9394 features a long open assembly

time while Hysol 9377 features high compressive strength with the ability to resist microcracking. Hysol EA 9394 is a high compressive strength, filled adhesive that can also serve as a bonding adhesive or potting material. Hysol 9377 has lower adhesive properties and has been developed specifically for liquid shim applications. Both products possess the important feature that they cure at room temperature.

Manufacturers of aerospace composite parts also desire aerodynamically smooth surfaces. This is more difficult with composites and therefore a complete line of epoxy-based composite surfacing films have been developed which provide protection for the composite surface while providing a high quality paintable surface off the tool. Henkel's products for this application include SynSkin 9837.1 and Hysol PL 795-1SF. Fig. 5 compares a surfaced and unsurfaced composite. Both of these products can be laminated with lightweight screens of aluminum or copper ranging from 73 to 195 g/m<sup>2</sup> (0.015 to 0.04 pounds per square foot). The screens provide composite assemblies with protection from zone 1 to 3 lightning strikes.

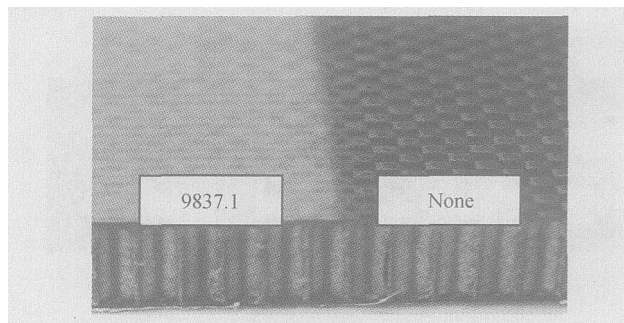


Fig. 5 EA 9837.1 surfacing

As with any composite design, repair is an area that must be defined. Henkel provides several wet lay-up resins, which are low viscosity paste adhesives used to impregnate graphite fiber for repair. Two of the most popular products are Hysol EA 9390, qualified and used on Boeing aircraft, and Hysol EA 9396. Hysol EA 9390 provides high temperature performance and must be cured under elevated temperatures. Hysol EA 9396 features room temperature cure capability but also cure at elevated temperatures. Typical aircraft repairs desire adhesives that

cure at 93 °C or below to absorb water from ingressing into the repair area and to minimize secondary damage from this water. In addition, Hysol provides several repair pastes such as Hysol EA 9360 or Hysol EA 9394 which can be used as an adhesive for cured patches. Both of these adhesives feature room temperature cure and are used in premeasured packaging.

With respect to fabricating composite structure on composite or metal tools/mandrels, it is vitally important to utilize a mold release material. Mold releases actually provide a surface from which the part will debond from the tool after cure. Henkel provides the FreKote line of mold releases and our most common products are FreKote 44 and FreKote 700. Both of these products provide a good release surface so that the part will readily release from the tool.

1.3 Nacelle Structure

The structure surrounding the engine demands some of the most extreme requirements for epoxy film adhesives. This structure includes the inlet and the cowl doors shown in Fig. 6. Adhesives used in the fabrication of composite or metal honeycomb stiffened nacelles, must withstand 1000 to 6000h of thermal aging at either 149 °C or 177 °C and still retain high levels of adhesive performance. Further, these materials are designed in both supported fabric versions and unsupported versions. The unsupported versions are subject to a process called reticulation whereby a hot air knife is used to coat the adhesive only on the ends of the core cells. See Fig. 7. This allows an open cell structure in the finished part that is used for sound suppression while allowing a lighter weight film adhesive to be used. Henkel’s most common products in this family include Hysol EA 9689, Hysol EA 9657 and Hysol PL 780-1.

2 Epsilon Systems

2.1 Attributes

Benzoxazine chemistry has several unique features that are desirable for composite matrix resins and adhesives. Some of the significant features of Epsilon formulations are ambient temperature storage for up to one year without a change in handling or

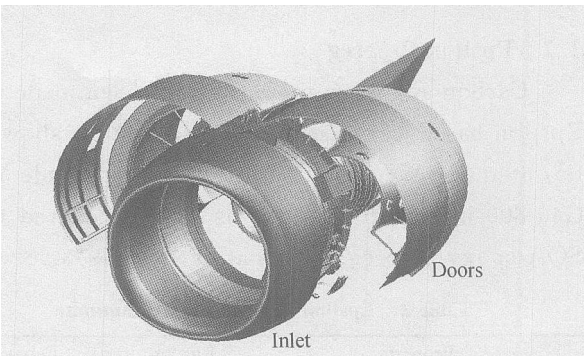


Fig. 6 Engine nacelle

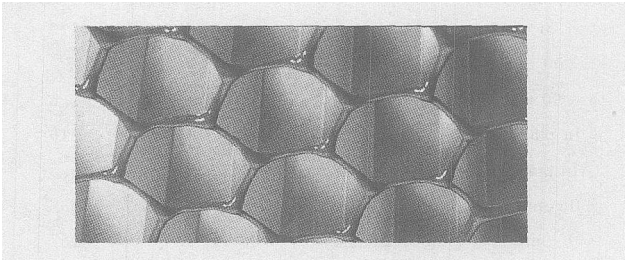


Fig. 7 Reticulated 9689 film adhesive

mechanical properties. Low equilibrium moisture absorption of about 1.5% based on neat resin provides for very good hot/wet properties. Shrinkage during cure is much lower than state-of-art (SOA) epoxy. Epsilon also adheres well to fibers. This chemistry is easily modified to achieve a wide range of processing and performance properties. The viscosity is easily modified and this provides the opportunity to provide resins for prepregs, as well as low viscosity resins for use in advanced composites processes. Several of these processes exist and there are numerous additional variations. VaRTM resins require viscosities in the 50 to 100 mPa • s range while matrix resins for resin film infusion (RFI) need viscosities in the 100 to 500 mPa • s range at the preform infusion temperature. Table 1 shows some examples of this flexibility for a neat resin formulation (no fiber) compared to an SOA toughened epoxy matrix resin for carbon composite.

Table 1 Epsilon neat resin properties

Property	Epsilon	Epoxy
Volume fraction of shrinkage/ %	– 1.8 ~ 1.0	5
Mass fraction of water uptake/ %	1.3 ~ 2.1	3.5
T <sub>g</sub> @ G’ onset/ °C	160 ~ 267	140
Compressive strength/ MPa	214 ~ 234	221
Compressive E/ GPa	4.1 ~ 4.7	3.5
G <sub>1c</sub> / (J • m <sup>-2</sup> )	160 ~ 500	350

2.2 Epsilon Prepreg

Carbon and glass prepregs have been made using Epsilon-based formulations. Table 2 below shows data obtained from unidirectional prepreg made using G40-800 intermediate modulus fiber compared to an SOA epoxy prepreg. Laminate  $V_f$  was 59%.

Table 2 Epsilon/ IM carbon UD laminate

Property	Epsilon	Epoxy
$T_g@G'$ onset/ °C	192	188
0 tension strength/ MPa	2520	2820
0 tensile modulus/ GPa	162	173
90 tension strength/ MPa	62	75
90 tension modulus/ GPa	9.3	7.6
In plane shear strength/ MPa	75	110
In plane shear modulus/ GPa	5.1	5.5
0 compressive strength/ MPa	1580	1600
0 compressive modulus/ GPa	170	157
OHC strength/ MPa	320	330
OHC strength wet* / MPa	255	262
ILSS strength/ MPa	96	112
CAI strength/ MPa	290	290

\* Moisture saturation at 0.53 weight %

The laminate was cured for 120 min @ 180°C using 6 bar pressure. Review of the data shows Epsilon to compare favorably with epoxy.

2.3 Epsilon Laminate Morphology

A cured laminate cross-section is shown in Fig. 8. This view obtained from a stained laminate using optical microscopy shows a second phase separation morphology. The toughener has an average particle size of approximately 1 micron. The phase separated toughener is homogeneously distributed in the resin rich areas and within the fiber bundles.

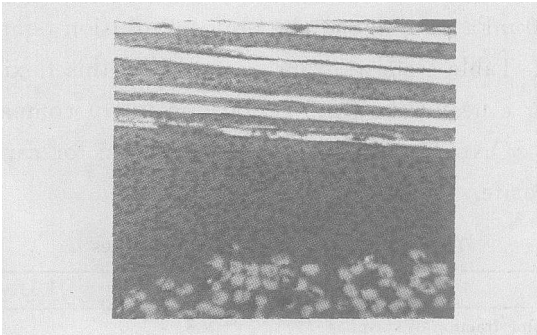


Fig. 8 Epsilon laminate morphology

2.4 Epsilon Adhesive

An adhesive film based on Epsilon chemistry was tested for high temperature performance. This film

adhesive alone gave a cured onset  $T_g$  of 260°C. The film adhesive weight was 440g/m<sup>2</sup> (0.090 pounds per square foot) and it contained a nonwoven support. Epsilon laminate substrates were used for substrate. The autoclave cure schedule was 90 min @ 180°C using 2 bar pressure plus a 60min @ 232°C free standing post cure in a forced air oven. Table 3 below shows tensile lap shear at several temperatures.

Table 3 Adhesive performance

Property	Epsilon
$T_g$ , dry, $E'$ onset/ °C	260
Tensile lap shear@ 23°C/ MPa	20.4
Tensile lap shear@ 204°C/ MPa	10.6
Tensile lap shear@ 232°C/ MPa	5.9

Failure mode for the tensile lap shear was cohesive in the adhesive for the 23°C and 204°C tested samples. The 232°C tested samples failed in the laminate.

2.5 Epsilon Syntactic

A syntactic paste was formulated and evaluated for performance in 9 cm deep core. After the cure was complete the potting material had a low porosity appearance and very little discoloration due to exotherm. See Fig.9. This result is due to the Epsilon resin having very low exothermic heat evolution during cure compared to epoxy.

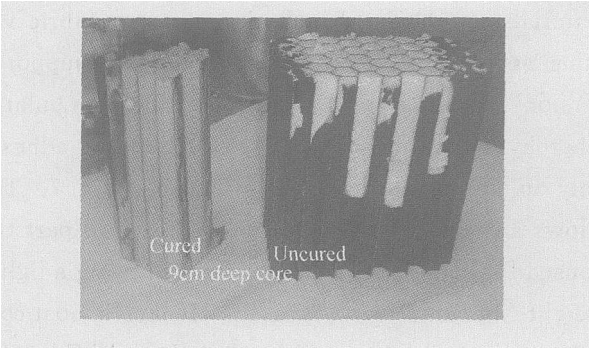


Fig. 9 Syntactic core potting

3 Summary

Henkel has a wide range of adhesives and composite products that are widely accepted and used in the aerospace industry for bonding and laminate fabrication. New products based on a newly developed chemistry show properties that are applicable for use in aerospace structures.