BENZOXAZINE MATRIX RESINS FOR STRUCTURAL COMPOSITE APPLICATIONS

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ABSTRACT

Benzoxazine resins offer significant potential as matrices for structural composites because of their high temperature properties, low moisture absorbance, dimensional stability, and flammability performance. Results are presented on a family of compatible, formulated benzoxazine resins. These include resins for use in structural prepregs, liquid molding and film adhesives.

INTRODUCTION

Benzoxazine resins have significant potential for use in structural applications [1, 2]. Benzoxazines offer high temperature performance, low moisture absorbance, dimensional stability, good flammability properties, and the potential for ambient storage [3, 4, 5]. Established resin systems such as phenolic, epoxy and bismaleimide (BMI) have demonstrated excellent performance characteristics in a wide range of demanding applications. Benzoxazine resins can have high glass-rubber transition temperature (Tg), and low moisture absorbance resulting in high service temperatures. The increasing use of composites in structural applications and stricter flammability requirements drive the need for improved flammability performance. Lower toxicity requirements have narrowed the scope of options in addressing flammability requirements for interiors. Epsilon benzoxazine resins have shown excellent flammability performance, even meeting current aircraft interiors requirements [5]. To address the need for improved performance in multiple areas Henkel has developed a family of 'Epsilon' benzoxazine resins based on a single chemistry platform. Different Epsilon formulations meet various processing and application needs: structural prepregs, liquid resin molding and adhesives.

This approach has the advantage that the family of products is tailored to be fully compatible and may be used with each other in co-cure applications.

STRUCTURAL PREPREGS

Carbon fiber reinforced prepregs were manufactured using an Epsilon resin formulated for structural matrix applications. The prepreg was a unidirectional carbon fiber tape with intermediate modulus carbon fiber at a fiber areal weight of 190 g/m2 and a resin content of 35 %. Mechanical test results were normalized to the nominal cured ply thickness of 0.19mm. Laminates were autoclave cured at 180 °C for 3-hours. Resin dominated properties are the major area of interest since this is where we will see the effects of using a benzoxazine resin. Two properties of particular interest are the open-hole compression (OHC) strength and compression after impact (CAI) strength. These properties represent the design limiting performance in many applications. The test methods were:

CAI: ASTM D7137 with 30 J impact energy, Lay-up (+45/0/–45/90)3S
OHC: ASTM D6484, Lay-up (+45/0/–45/90)2S

The results are shown in Figure 1. The room temperature OHC and CAI strengths at zero storage time are similar, indicating that design performance in the presence of defects is balanced. Matrix dominated properties of most resin systems are reduced at higher temperatures and after moisture conditioning, due to plasticization of the matrix. The 98% retention of open-hole compressive strength at 82 °C compared to

room temperature demonstrates that for many service conditions no change in design property is required at a typical maximum service temperature compared to room temperature. The prepreg was evaluated after 6- and 9-month storage at room temperature. The prepreg retained good tack and drape after 6-months. The tack and drape were reduced after 9-months and the material could be used with slight warming. There is a small reduction in CAI, and a slight increase in OHC with storage time, and these changes are small compared to the control.

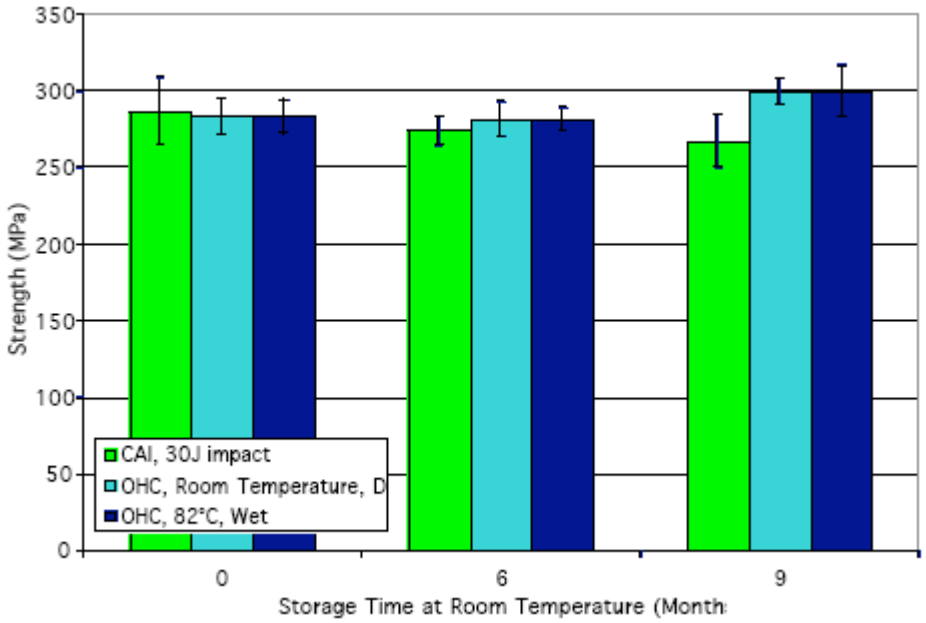

Figure 1. Compression after impact and open-hole compression of Epsilon prepregs.

Another aspect of resin dominated performance is the effect of fluid environments. In-plane shear is particularly sensitive to the effects of aggressive fluids. The same Epsilon resin was evaluated with a standard modulus carbon plain weave fabric at 193g/m2, in a lay-up of (±45)2S using ASTM D3518 method. Figure 2 shows the effects of various environments on in-plane shear strength and modulus. The in-plane shear modulus of the control was 4.5 GPa, and the in-plane shear strength 122 MPa. The results demonstrate the excellent performance in fluid environments.

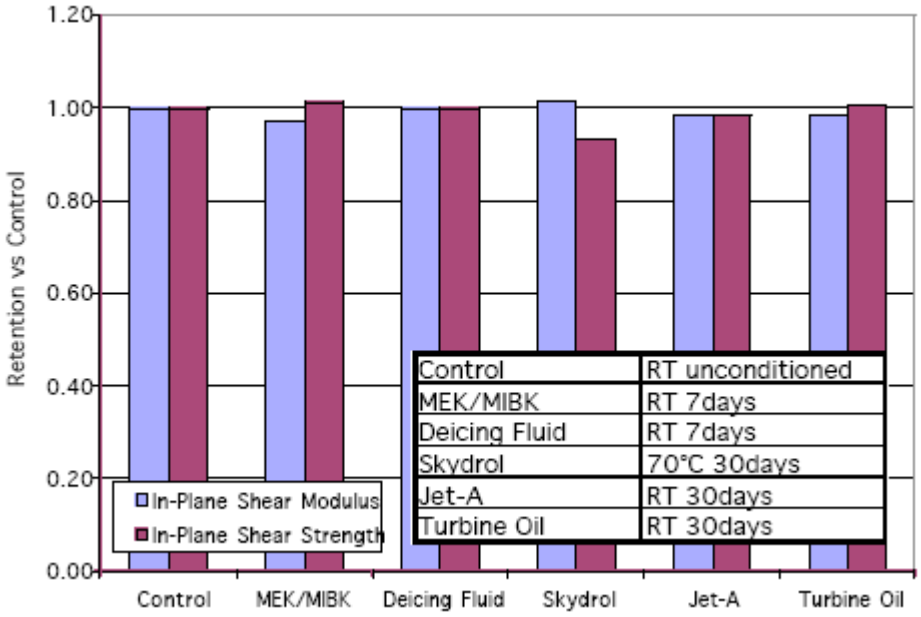

Figure 2. In-plane shear strength and modulus after conditioning in fluid environments

LIQUID RESINS

Epsilon liquid resins have been developed for resin transfer molding (RTM) and vacuum assisted RTM (VARTM) processing (6). Epsilon 99110 resin has a balance of processing and structural performance. Epsilon 99120 is intended for use where it is not practical to use ex-situ toughening, such as with 3-D performs, and where the highest toughness is required. A compatible binder, Epsilon 99900, provides fabric preforming capability and adds toughness to the composite. The resins were infused into the reinforcement at 110 °C. The resins and composites were cured at 180 °C for 90 minutes. Properties of two resins are shown in Table 1. Both resins have Tgs which provide service temperature of over 119 °C after wet conditioning (6). Epsilon 99120 has higher resin elongation and fracture toughness, which results in composite CAI strength comparable to prepreg systems, even without a binder.

Table 1. Properties of Epsilon Benzoxazine Liquid Resins

Property	Units	Epsilon 99110	Epsilon 99120
Resin Properties			
Tg (DMTA G' Onset)			
Dry	°C	191	180
Wet (72-hour water boil)	°C	161	147
Tensile Modulus	GPa	3.7	3.4
Tensile Strength	MPa	97	106
Tensile Elongation	%	1.5	4.6
Fracture Toughness G_{1C}	J/m^2	112	511
Composite Properties[1]			
CAI Strength, No binder	MPa	201	241
CAI strength, 10% Binder[2]	MPa	276	290

1. Standard modulus, plain weave, 193g/m^2, $[(\pm45)(0/90)]_{6S}$, VARTM Processed
2. Binder: Epsilon 99900

ADHESIVES

Epsilon benzoxazine film adhesives have been developed for assembly of Epsilon composites. An Epsilon film adhesive with an areal weight of 250 g/m2 and a non-woven glass support scrim, was cured at 180 °C for 180 minutes, the same cure cycle as used for the prepregs. The Tg of the adhesive in the as molded state is 203 °C, and after 72-hour water boil it is 176 °C. Adhesive properties are shown in Figure 3. These included secondary bonding with aluminium and Epsilon composite substrates, and co-cure with Epsilon composites. An impregnated peel ply, Hysol® EA9895, was used for the surface preparation of the pre-cured composite. The room temperature adhesive bonding properties are comparable to those of current epoxy structural film adhesives. The single lap shear strengths with the co-bonded composite are comparable to the secondary bonded results, confirming the compatibility of the adhesive and prepreg matrix resin. The results at 149 °C show high retention of room temperature properties. In the case of the flatwise tension there is no reduction at 149 °C compared to room temperature. These results demonstrate the high temperature capabilities of the Epsilon benzoxazine for adhesive bonding applications.

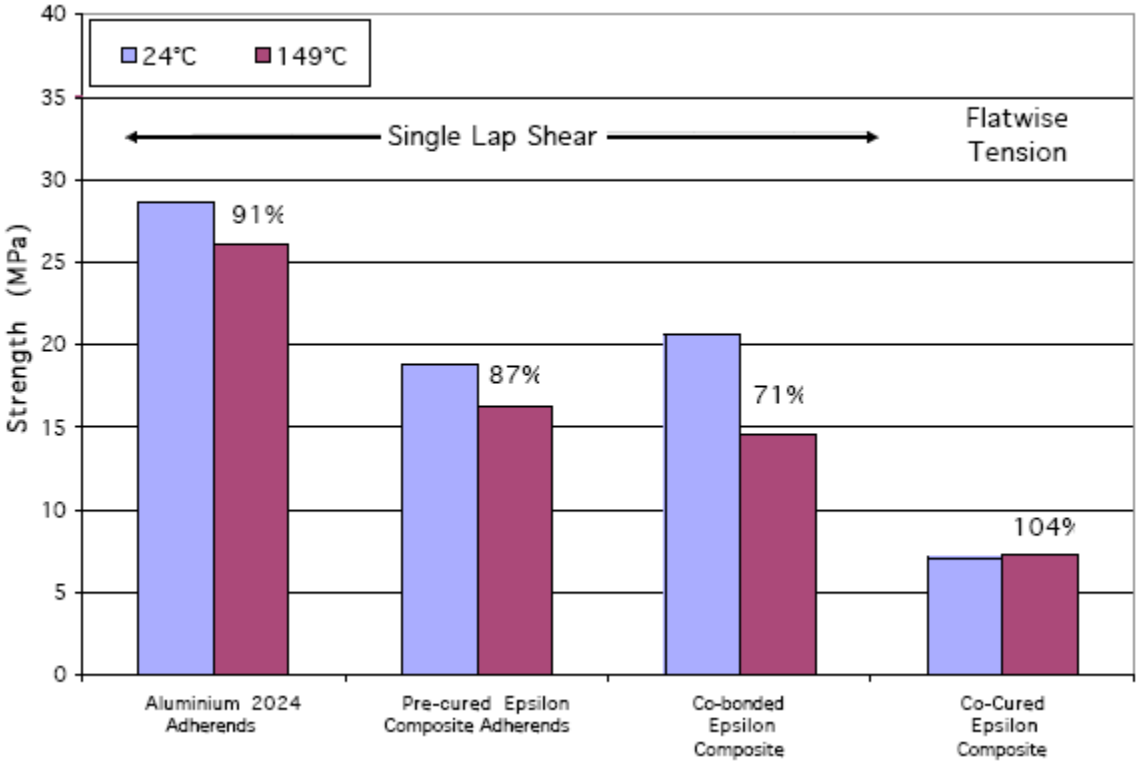

Figure 3. Properties of Epsilon benzoxazine film adhesives

CONCLUSIONS

A family of compatible Epsilon benzoxazine resins have been developed which are complementary to existing composite matrices. The results demonstrate that the composites manufactured with Epsilon benzoxazine resins possess a combination of high damage tolerance, retention of properties in hot-wet conditions, and resistance to aggressive fluids. The compatible benzoxazine film adhesives have performance equivalent to epoxy adhesives at room temperature accompanied by high retention of performance at 149 °C, in both secondary bonding and cocure applications. Therefore Epsilon benzoxazine resins offer opportunities for extending the performance of existing resin systems to improve high temperature performance and offer weight reduction.

Henkel Excellence is our Passion

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