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NOVEL RESIN SYSTEMS WITH SUPERIOR PROCESS AND PERFORMANCE

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SUMMARY

Loctite Aerospace has developed an alternative resin system to epoxy for structural aerospace applications. The objectives were to develop a broad base resin with excellent process characteristics and higher temperature performance. The notable resin attributes are ambient stability, near-zero curing shrinkage, high compression strength and modulus, and an adjustable viscosity profile suitable for advanced processes, such as resin transfer molding (RTM), vacuum-assisted RTM (VaRTM) and resin film injection (RFI). Additionally, this 180°C cure resin system gives a very good combination of hot/wet glass transition temperature (T_g), toughness and modulus. This paper will explore the application of this system as a matrix resin for prepreg and other advanced composite processes.

1. INTRODUCTION

Epoxy has been widely used in high performance composites for aerospace applications. Factors such as resin cost, processing methods, materials strength and flexibility have limited the epoxy systems applicability. The state-of-art high structural performance prepregs are expensive. Toughened epoxy systems can only offer a composite with a 140^{o}C hot/wet T_g and the composite interlaminar shear strength (ILSS) loss is more than 50 percent at 120^{o}C [1]. Fire, Smoke and Toxicity

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(FST) Requirements have prevented epoxy use in airframe interior applications. Today, it is a challenge for a high performance epoxy system to exhibit a service temperature of 160°C at a hot/wet condition, good toughness and processing ease. High temperature performance resins including bismaleimide (BMI) and phenylethynyl imide (PETI) have limited use in the aerospace industry primarily because of the high resin cost. These resins also have complicated processing parameters. For example, a RTM injection temperature of 288°C and a curing temperature as high as 370°C is required to obtain a T_g of 250-300°C [2]. Moreover, these resins are brittle and toughness improvement is difficult.

Benzoxazine is a newly developed thermosetting resin and can offer the best performance at competitive costs with commercial resin systems. The chemistry, synthesis, physical and mechanical characteristics have been studied by several research groups [3-5]. However, a benzoxazine resin system that can meet aerospace material processing and high performance requirements has not been reported.

Loctite Aerospace has intensively worked on benzoxazine design chemistry, resin formulation, processing characteristics and performance development. The three 180°C cure benzoxazine systems discussed here have the following special attributes compared to the state-of-art prepreg resins.

Attributes	**Benefits**
Ambient storage	- Lower handling cost, longer assembly time
Near zero cure shrinkage	- Longer service life, less residual stress
Low density	- Lower composite weight and resin cost
Low water absorption	- High hot/wet service capacity
Adjustable viscosity	- Suitable for multiply processes (RTM, RFI, prepreg, etc.)

The cured resins and composites provide an excellent combination of properties including high dry and hot/wet T_g, high toughness, high compressive strength and modulus, good solvent resistance and FST properties.

2. EXPERIMENTAL AND RESULTS

2.1 Resin Characterization

The three formulated benzoxazine systems evaluated are I, II, and III. For comparison, an epoxy resin formulation comprised of 100 parts (by weight) of Vantico's Araldite MY721 resin and 44 parts of 4,4'-diamino diphenyl sulfone (DDS) hardener was used.

Resin viscosities were measured with Rheometrics Dynamic Analyzer (RDA) at a ramp rate of 2^{o}C/min. Ambient stability was confirmed by monitoring II resin for 12 months at ambient storage with no observable change in the viscosity profile.

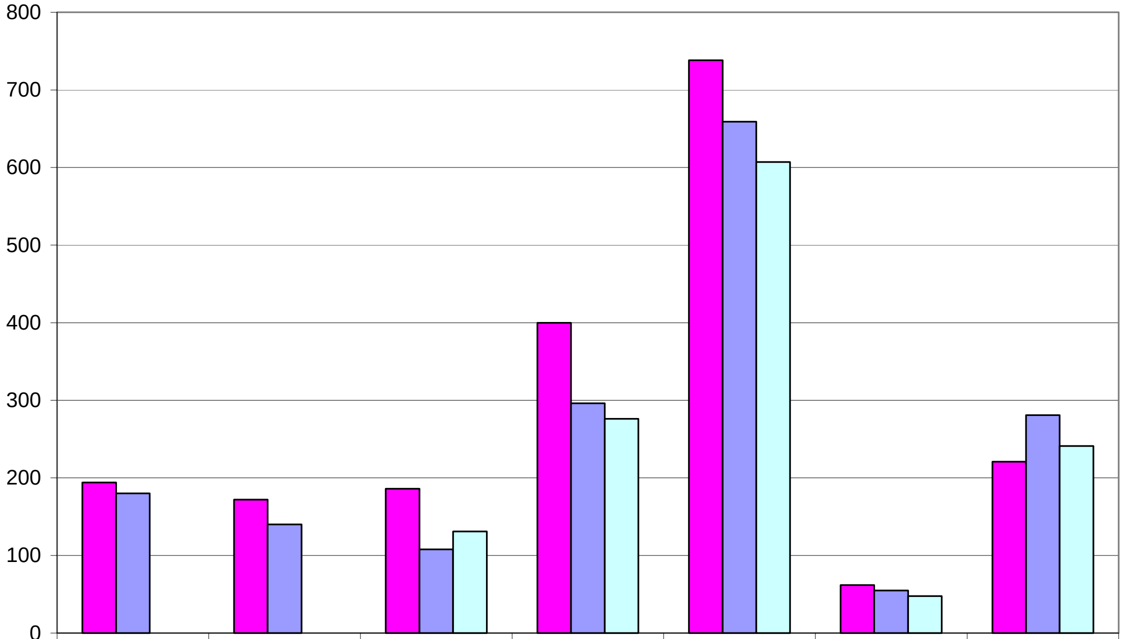
Differential Scanning Calorimetry (DSC) was performed with Perkin Elmer DSC 7 at a ramp rate of 10^{o}C/min. Resins were cured in oven or autoclave using a ramp of 2^{o}C/min to177^{o}C, holding for 180 minutes and cooling at 3-5^{o}C/min. A Rheometrics Dynamic Mechanical Thermal Analyzer (DMTA) with a ramp rate of 5^{o}C/min. was used to obtain the T_g by the storage modulus at onset. Hot/wet T_g and water gain were obtained using specimens boiled in water for 72 hours. Densities were determined by water displacement. Shrinkage was calculated by the volume loss percentage based on density before and after cure. The flexural and compressive properties were determined in accordance with ASTM D790 and D695.

Neat Resin	I	II	III	MY721/DDS
Density, g/cm^3	1.20	1.18	1.09	1.24
Shrinkage, %	-1.8	-0.5	1.0	-9.0
H, J/g	-320	-343	-141	-711
T_g (G' onset),°C	190	199	197	230
T_g hot/wet,°C	159	178	190	174
T_g drop, %	16	11	4	25
Moisture Uptake, %	2.1	1.3	1.5	5.1
Comp. Strength, Mpa	214	234	221	170
Comp. Modulus, Gpa	4.2	4.7	4.1	3.5
Flexure Strength, Mpa	103	124	110	131
G_{IC}, J/m^2	245	158	403	105

Table 1: Neat Resin Property Comparison

2.2 Composite Fabrication and Characterization

I resin was used to make T300 3K PW70 190 gsm prepreg. Composite laminates were assembled, cured and tested according to Boeing BMS 8-276. The key mechanical properties evaluated were open hole compression strength (OHC, Mpa), in-plane shear strength (IPS, Mpa), compression strength (CS, Mpa) and modulus (CM, Gpa), CAI (Mpa), dry and hot/wet T_g(^{o}C).



	Tg	Tg H/W	IPS	OHC	CS.	CM	CAI
■ el	194	172	186	400	738	62	221
■ 977-2	180	140	108	296	659	54.9	281
□ Req.			131	276	607	47.6	241

Figure 1: I/ T300 3k PW70 Composite Properties Compared to Cytec 977-2/ 6k HTA 5HS Composite [1] and BMS8-276 Requirement

RTM laminates were made using I and II resins with Cramer 445 370 gsm fabric. The injector and the 350 x 350 mm dimension mold with fabric preform were preheated to 120^{o}C. Resin was preheated to 80^{o}C and poured into the injector. Injection started with 0.3 bar pressure and gradually increased to 6 bars before the injection was finished (~20 min). The mold was heated to 180^{o}C at 2^{o}C/min. and held for 180 minutes then cooled to ambient.

Laminates were scanned ultrasonically (c-scan) to confirm quality. V_f was determined by acid digestion following ASTM D3171. Specimens were prepared and tested in accordance with Airbus ASTI specifications. FST for II composite is being tested.

Property	Conditioning	Test condition	Req.	I	II
V_f, %			60	59	60
ILSS, Mpa	MEK/RT/1h	RT	60	61	63
	Water/100°C/2h	70°C	TBD	55	62
	Dry	RT	60	57	67
	Dry	120°C	28	47	53
	70°C/85% R.H.	70°C	TBD	48	57
T_g, (G' onset), °C	Dry		160	192	211
	70°C/85% R.H.		140	169	185
IPS strength, Mpa		RT	70	102	146
IPS modulus, Gpa		RT	4.7	3.2	4.6
CAI, Mpa		RT	200	232	205

Table 2: RTM Composite Properties with Cramer 445 Fabric

3. DISCUSSION

I combines a reasonable toughness and high temperature performance. The composites hot/wet T_g (G' onset) of 170^{o}C make it superior to high performance epoxy systems and meet the need for a 180^{o}C cure system with 160^{o}C or higher service temperature even at a hot/wet condition. The composite CAI (240 Mpa after a 25 joule impact) and high OHC show the high performance required for aerospace structural applications. The ILSS loss of less than 20 percent versus epoxy ILSS loss of more than 50 percent make it unique and very attractive. The resin is suitable for prepreg, RTM, VaRTM, and RFI processes.

II was formulated for RTM applications with low viscosity and high cured T_g. The resin viscosity is 50 mPa.s at the injection temperature. The viscosity doubles after 2 hours at 120^{o}C or 4 hours at 110^{o}C. Using one hour post cure at 230^{o}C, the neat resin T_g (G' onset) increases to 250^{o}C, which is beyond epoxy capacity. BMI or PETI need higher cure temperatures to obtain this level of T_g. This makes II an attractive material for tailoring T_g using a post cure.

III was formulated for high performance prepreg applications. The resin has a low density of 1.09 g/cm^3 compared to a typical aerospace epoxy formulation with 1.26-1.31 g/cm^3. The resin has a very small T_g drop (<4%) with an incredible hot/wet T_g of 190^{o}C while the G_{IC} is high at 400 J/m^2. Prepreg and composite properties are under investigation.

4. CONCLUSIONS

Loctite Aerospace has developed benzoxazine systems to compliment on epoxy systems. These systems offer high temperature performance and meet the demanding process requirements of advanced processes for aerospace structural applications.

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