NOVEL FST THERMOSET SOLUTION FOR LIGHTWEIGHT COMPOSITE AEROSPACE INTERIOR APPLICATIONS

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ABSTRACT

A new developed high-performance flame retardant resin system for use to manufacture aircraft interior parts by RTM or infusion will be introduced in this paper. The inherent FST (Flame, Smoke and Toxicity) properties of this resin system come from its chemical structure and its high cross-link density as opposed to conventional flame retardant systems which rely on the presence of inorganic fillers and additives. This new resin system meets the FAR 25.853 vertical burn, smoke and toxicity requirements with both carbon and glass fiber reinforcement in various thickness configurations. The mixed two-component latent system with low viscosity at low working temperatures allows the production of small and large complex parts. The polyaddition reaction was tailored for cross-linking to yield quality composites without releasing any volatile by-products and suitable for VOC emission free working environment. This novel high-performance solution provides what may be considered as a new and improved value proposition for aerospace designs, providing a preferred alternative to metal in structural applications and phenolics in non- and semi-structural applications.

1. INTRODUCTION

Traditionally, phenolic resins are used in a variety of aerospace interior applications mainly due to their low cost and good flame, smoke, and toxicity (FST) performance [1-4]. However, as the curing is based on a condensation reaction mechanism, water and formaldehyde are released during high temperature curing process, which leads to voids and surface pinhole in the final laminate parts, and generates concerns with regards to environmental, health and safety (EHS) issues due to hazardous chemical exposure. Benzoxazine thermoset resin systems, such as ARALDITE® 35710 FST and ARALDITE® FST 40010/40011 resin systems have been developed by Huntsman Advanced Materials for aerospace and other transportation interior application [2, 5]. These benzoxazine systems offer inherent low fire, smoke and toxicity (FST) properties. Additionally, as the benzoxazine curing is based on ring-opening polymerization mechanism, there are no volatile by-products, which results in high quality parts with very low void content. However, these benzoxazine resin systems are solid or semi-solid at room temperature, high temperature processing and curing are required.

To improve cost efficiency and environmental performance, the aerospace industries are continually seeking weight and structure optimization in aircraft design with an increasing focus

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on the role of advanced composites as seen in the recent international aerospace conferences. Huntsman Advanced Materials has been considered a pioneer in the advanced composite technology and most recently has launched ARALDITE® FST 40002 / 40003 resin system, an entirely new high-performance and inherently flame-resistant solution for RTM and infusion processing [6].

ARALDITE® FST 40002 / 40003 resin system is a radically different development that provides a unique combination of good fire, smoke and toxicity (FST) performance, good mechanical properties and user-friendly composite processing conditions, which allows efficient production of interior carbon and glass composite parts with maximized weight savings. As opposed to conventional flame retardant systems which rely on the presence of inorganic fillers and additives, Araldite® FST 40002 / 40003 resin system is an unfilled system, where the inherent FST properties of the system come from the chemical nature of the network and its high cross-link density. As compared to phenolic resins which cure via a polycondensation reaction and are used for non- and semi-structural applications, this new system cures via a polyaddition reaction without releasing any volatile by-products. This feature results in improved composite parts quality, a cleaner and healthier manufacturing environment for the operators and by being VOC emission free, it also makes the use of closed mold processes possible. Resin processing rheology, reactivity and curing characteristics of this resin system have been evaluated. Performance advantages including both net resin and composite system are investigated and discussed.

2. EXPERIMENTATION

2.1 Raw Materials

The study uses the ARALDITE® FST 40002 and ARALDITE® FST 40003 resin system. This resin system is designed primarily for aerospace and other transportation interior applications. Style 7781 glass fabric, G1157 UD and G0926 carbon fabrics are used for laminate preparation and testing. The mix ratio for the ARALDITE® FST 40002 / 40003 system is shown in Table 1.

Table 1. Mix ratio of ARALDITE® FST 40002 / 40003 resin system

Components	Parts by weight	Parts by volume
Araldite® FST 40002	100	100
Araldite® FST 40003	25	23

2.2 Sample preparation

2.2.1 Mixing and degassing of ARALDITE® FST 40002/40003 resin system for net casting and infusion

a) Assemble apparatus inclusive of flask, stirrer and thermocouple and vacuum test prior to charging material(s). (Vacuum target is < 5 mbar).

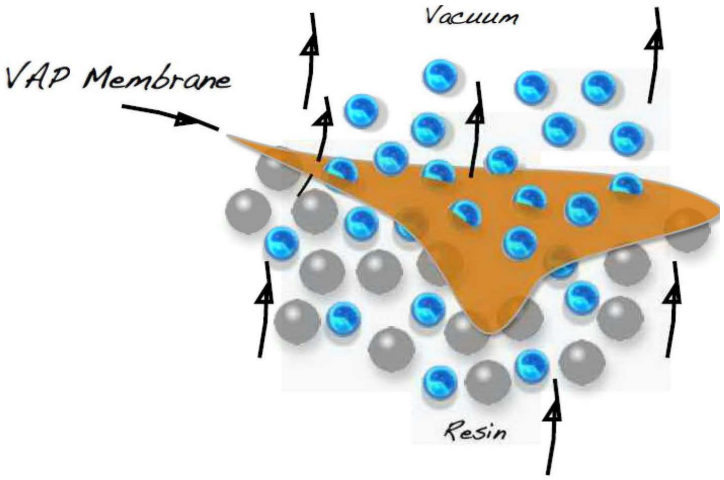
b) Properly secure flask in heating bath. NOTE: Proper alignment is key to achieve vacuum target.
c) Set the oil bath temperature set point to 50 ºC and turn on the oil bath heater.
d) Charge ARALDITE® FST 40002 to the flask.
e) Degas under vacuum (< 5 mbar) with stirring for 15-20 minutes (note: watching carefully for foaming).
f) Charge ARALDITE® FST 40003 to the flask (note: Preheat ARALDITE® FST 40003 in 70 °C oven for 1 hour before use).
g) Mix and degas under vacuum (< 5 mbar) for 40-45 minutes (note: watching carefully for foaming).
h) The resin mixture is ready for net casting and infusion.

2.2.2 Preparation of neat resin plaques.

The resin mixture was poured immediately into pre-heated (100 ºC) glass molds. The molds were cured in an air circulating oven for 1 hour at 100 ºC + 1 hours at 120 ºC + 2 hours at 180 ºC before cooling down and demolding.

2.2.3 Preparation of laminates.

Glass and carbon laminates were made by infusion process. To make high quality parts, a special VAP membrane is used during the infusion process. The membrane allows vacuum to go through without resin, therefore the vacuum can be applied during infusion and cure over the whole surface of the part. The principle is described in the scheme below:



To ensure a void free laminate, it is recommended to use a vacuum pressure of < 5 mbar for the infusion. Use the resin mixture immediately after degassing. If it is difficult to see the resin flow front during infusion, then the infusion can be followed by monitoring the weight of resin going into the stack. The resin inlet clamp can be closed when resin intake is < 5 g/min.

a) Prepared mold with fiber stack should be heated at 90 ºC under full vacuum for 2 hours in the oven before infusion.
b) The mold can be cooled down under full vacuum to 60-70 ºC for the infusion process.
c) Open inlet clamp and start infusion.

d) The inlet clamp can be closed in 10 minutes (or when resin intake is < 5 g/min).
e) The mold should now be heated according to cure cycle (100 ºC/1 hour + 120 ºC/1 hour). Note: The vacuum MUST BE applied during the cure cycle.
f) The part may be de-molded before carrying out the post-cure.
g) Post cure at 180 ºC for 2 hours.

3. RESULTS

3.1 Reactivity and curing characteristics

ARALDITE® FST 40002 / 40003 resin system has a low reaction energy of about 220 J/g which eliminates bulk exothermic safety issues as well as enables large thickness composite part production. The gel time of the Araldite® FST 40002 / 40003 resin system is shown in Table 2.

Table 2. Gel time of ARALDITE® FST 40002 / 40003 resin system

Gel time (10 grams by Sunshine Gel-timer)	Minute
70 °C	96.0
80 °C	23.1

ARALDITE® FST 40002 / 40003 resin system shows snap-cure behavior which allows fast Tg and interlaminar shear strength (ILSS) development. Large parts can be demolded after pre-cure conditions of one hour at 100 °C followed by one hour at 120 °C. This system also allows small to medium part production with very high output as parts can be demolded after 5 minutes at 150 °C. Typical cure cycles are shown in Table 3.

Table 3. Typical cure cycles of ARALDITE® FST 40002 / 40003 resin system

	Typical cure cycles
For large part	1 hour/100 ºC + 1 hour/120 ºC + 2 hours/180 ºC
For small/medium part	5 min/150 ºC or 20 min/120 ºC + 2 hours/180 ºC

3.2 Viscosity and Processing Characteristics

ARALDITE® FST 40002 / 40003 resin system exhibits a low viscosity even at 25 ºC. The temperature dependence of initial mix viscosity (per ISO 2555) is shown in Figure 1. This resin system shows much lower viscosity (40 cps at 65 ºC) compared to a typical bisphenol-A benzoxazine (viscosity for ARALDITE® MT 35610 bisphenol-A benzoxazine is 100-1,000 cps at 125 ºC) and bisphenol-F benzoxazine (viscosity for ARALDITE® MT 35710 FST bisphenol-F benzoxazine is 20-100 cps at 100 ºC). This allows the end user to incorporate the resin system into infusion or resin transfer molding processes at lower temperature.

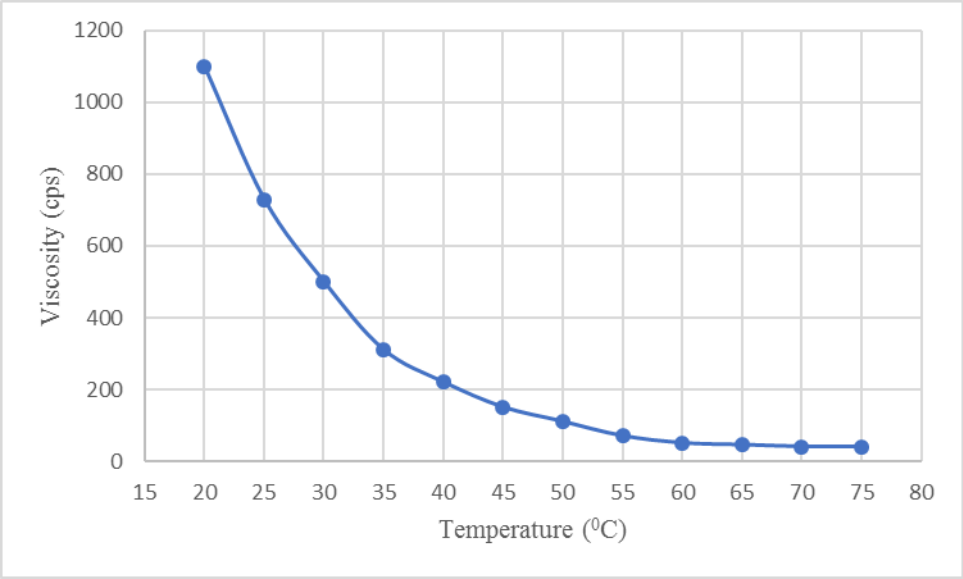


Figure 1. Initial viscosity vs temperature for ARALDITE® FST 40002 / 40003 resin system

The isothermal viscosity (per ISO 2555) of ARALDITE® FST 40002 / 40003 resin system at various temperatures is shown in Figure 2. The mixed two-component latent system with low viscosity at low working temperatures allows the production of small and large complex parts by infusion and resin transfer molding processes.

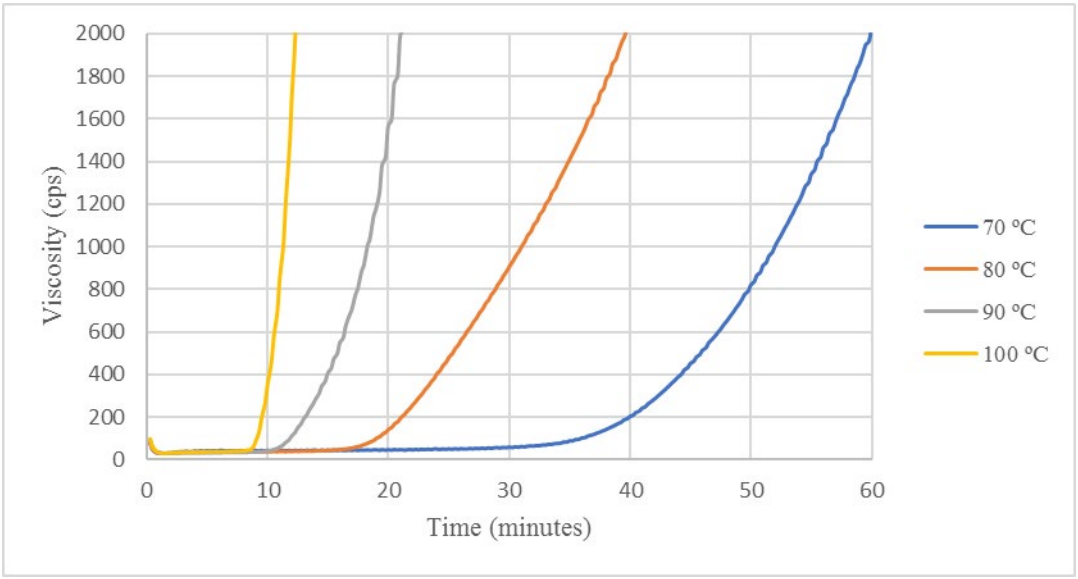


Figure 2. Isothermal viscosity of ARALDITE® FST 40002 / 40003 resin system at different temperature

3.3 Cured neat resin mechanical properties

Mechanical properties of the neat resin are summarized in the Table 4. ARALDITE® FST 40002 / 40003 resin system exhibits good toughness and has a K_{1C} of 0.85 – 0.95 MPa.√m and G_{1C} of

250-300 J/m^2, which is much higher than those of traditional phenolic resins [5] and higher than those of un-toughened epoxy resin systems.

Table 4. Mechanical properties of ARALDITE® FST 40002 / 40003 neat resin system

Properties	Test Method	ARALDITE® FST 40002 / 40003
Curing conditions	1 hour/100 ºC + 1 hour/120 ºC + 2 hours/180 ºC	
Tensile Modulus, MPa	ISO 527	2900 - 3100
Tensile Strength, MPa		95 - 105
Elongation at break, %		4.5 - 5.5
Fracture toughness K_{1C}, MPa.√m	ISO 13586	0.85 – 0.95
Fracture energy G_{1C}, J/m^2		250 - 300

3.4 Composite properties

Table 5 and Table 6 are summary of mechanical properties of laminates made with glass or carbon fiber and ARALDITE® FST 40002 / 40003 resin system. ARALDITE® FST 40002 / 40003 resin system develops dry and wet Tg of 270-280 °C and 180-190 °C respectively. Beside high Tg, high tensile strength and good toughness, when comparing the results presented here with reported data for typical phenolic composite in the literature [2, 5], ARALDITE® FST 40002 / 40003 laminates demonstrate significant increase in interlaminar shear strength (ILSS) (66-100 MPa for ARALDITE® FST 40002 / 40003 and 24-50 MPa for phenolic). With these advantages, ARALDITE® FST 40002 / 40003 resin system may be used in aerospace both of non- or semi-structural and structural applications.

3.5 Flammability, Smoke and Toxicity (FST) Performance

The ARALDITE® FST 40002 / 40003 resin system meets the FAR 25.853 vertical burn, smoke and toxicity requirements with both carbon and glass fiber in all thickness configurations as shown in Table 7. For heat release performance, only thin laminates (0.3 mm thick) made from Araldite® FST 40002 / 40003 pass the heat release requirements of FAR 25.853, this is due to ARALDITE® FST 40002 / 40003 resin system is an unfilled system, as described previously, the inherent FST properties of the system come from the chemical nature of the network and its high cross-link density, and is not based on additives or halogenated chemistry. According to paragraph (e) of FAR Title 14 Section 25.853, if the interior parts are out-of-the-way from the main passenger cabin, the heat release performance is not required. Therefore, ARALDITE® FST 40002 / 40003 resin system may be suitable for use in the interior parts that don't require heat release performance.

Table 5. Properties of ARALDITE® FST 40002 / 40003 cured glass laminate

Properties		Test Method	ARALDITE® FST 40002 / 40003 Glass Laminate (Glass 7781, Fiber volume content 50%)	
Curing conditions		1 hour/100 ºC + 1 hour/120 ºC + 2 hours/180 ºC		
Glass Transition Temperature		DMA ISO 6721	Dry	Wet*
	T_G onset, ºC		270 - 278	180 - 190
	T_G peak, ºC		290 - 300	255 - 265
Tensile Test	Tensile modulus – 0º, GPa	AITM 1.0007	22 - 24	
	Tensile strength – 0º, MPa		390 - 400	
	Elongation at break – 0º, %		2.0 – 2.2	
Interlaminar Shear Strength	ILSS, MPa	ASTM D2344	66 - 68	
Interlaminar Fracture Toughness	G_{IC}, J/m^2	AITM 1.0005	755 - 835	
	G_{IIC}, J/m^2	AITM 1.0006	2000 - 2700	

*3 days boiling water

Table 6. Properties of ARALDITE® FST 40002 / 40003 cured carbon laminate

Properties		Test Method	ARALDITE® FST 40002 / 40003 Carbon Laminate (Carbon UD G1157, Fiber volume content 60%)	
Curing conditions		1 hour/100 ºC + 1 hour/120 ºC + 2 hours/180 ºC		
Glass Transition Temperature		DMA ISO 6721	Dry	Wet*
	T_G onset, ºC		270 - 280	180 - 190
	T_G peak, ºC		290 - 300	255 - 265
Tensile Test	Tensile modulus – 0º, GPa	AITM 1.0007	123 - 128	
Interlaminar Shear Strength	ILSS, MPa	ASTM D2344	95 - 100	
Interlaminar Fracture Toughness	G_{IC}, J/m^2	AITM 1.0005	420 – 456	
	G_{IIC}, J/m^2	AITM 1.0006	774 - 794	

*3 days boiling water

Table 7. FST properties of ARALDITE® FST 40002 / 40003 glass and carbon laminates

		FAR 25.853 Requirement/Unit	ARALDITE® FST 40002 / 40003		
			CFRP G0926 0.3 mm Fiber volume 50%	CFRP G0926 2 mm Fiber volume 50%	GFRP 7781 0.3 mm Fiber volume 50%
FLAMMABILITY VERTICAL 12s (AITM 2.0002B)	Burn length	< 203 mm	88		48
	After flame time	< 15 second	9		15
	Drip flame time	< 3 seconds	0		0
FLAMMABILITY VERTICAL 60s (AITM 2.0002A)	Burn length	< 152 mm	82	47	65
	After flame time	< 15 seconds	0	6	0
	Drip flame time	< 3 seconds	0	0	0
HEAT RELEASE (AITM 2.0006)	Peak heat release	< 65 kW/m^2	63	85	45
	Total heat release	< 65 $kW.min/m^2$	32	90	25
TOXICITY FLAMING MODE (AITM 3.0005)	HCN	< 150 ppm	1		1
	CO	Ref	29		28
	NOx	< 100 ppm	2		2
	$SO_2 + H_2S$	< 100 ppm	1		1
	HF	< 200 ppm	0		0
	HCl	< 500 ppm	0		0
SMOKE DENSITY FLAMING MODE (AITM 3.0005)		< 200 Ds	23		16

4. CONCLUSION

Advanced composite processes and materials are essential for high-performance interior aerospace market. The ARALDITE® FST 40002/40003 resin system provides a unique combination of fire, smoke and toxicity (FST) performance, unfilled, low viscosity, low exotherm, latent, good mechanical performance and fast curing capability. This ARALDITE® FST 40002/40003 resin system allows the RTM and infusion processing to reach the new processing dimension especially the production of highly complex parts with a high level of function integration and significantly reduce the number of parts in many designs.

5. REFERENCES

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