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Next Generation Novolac Epoxy Vinyl Ester Resins for Heat Resistant Composites

ABSTRACT

Modified novolac epoxy vinyl ester resins are presented for composite applications demanding high heat resistance. These resins are liquid at room temperature, shelf-stable yet fast-curing, and compatible with a wide range of fabrication methods. Glass reinforced and carbon fiber reinforced composites derived from these high performance resins are constructed and tested for mechanical and thermal properties. The property retention at elevated temperatures of strength and modulus at elevated temperatures in these next generation resins exceeds today's commercially available highest performance vinyl ester resins.

1. INTRODUCTION

Vinyl ester resins have a long history of use in composite applications for harsh environments, as they combine excellent mechanical and thermal properties with very good corrosion resistance due in part to their cross-linking chemistry. Vinyl esters (VE) are frequently the resin of choice where fabrication methods compatible with unsaturated polyester resins (UPR) are preferred, but where the aforementioned properties of UPR fall short. Epoxy novolac vinyl ester resins (NVE) offer improved thermal performance over traditional bisphenol A vinyl esters and UPR. Similar to unsaturated polyesters and bisphenol A vinyl ester resins, NVEs are also cured with peroxides via a free radical mechanism using traditional fabrication methods. The methacrylate groups readily copolymerize with styrene upon initiation and propagation of the free radical reaction. The resulting high crosslink density in the finished composite part is a direct result of the NVEs multifunctional methacrylate polymeric backbone (figure 1), which contributes to premium thermal performance.

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Figure 1: Epoxy Novolac Vinyl Ester

Some applications for NVEs include corrosion resistant coatings, heat shields, chimney liners, parts for flue gas desulfurization, composite tooling, and other structural composite components where high heat resistance is mandated. The objective of this study was to design higher thermal performance novolac vinyl esters where these applications can be met according to the same processing methods used in UPR and traditional VE resins such as filament winding, hand lay / spray up, pultrusion, resin transfer molding, vacuum infusion, and compression molding. End use targets for these new heat-resistant resins include the applications listed above, as well as other market segments with demanding environments not serviced by existing VE technologies such as: downhole oil and gas production, power plants, under the hood automotive, and aerospace.

This report summarizes the details of several new higher temperature novolac vinyl ester resins (NVE) candidates, and compares them to today's premium commercially available novolac vinyl ester (F086). The general description of each NVE is shown in Table 1. Candidates are designed for extremely high heat resistance, ranging from very high cross link density, to toughened analogs with higher elongation. One candidate combines a brominated polymer backbone with the high crosslink density novolac vinyl ester functionality to provide high heat resistance with flame retardance (XR 4501). In each case, candidates are characterized and compared to the benchmark F086. Liquid properties are measured such as viscosity and gel time, and an investigation is initiated to determine utility of these new resins at high service temperatures and harsh environments. Measurements of retention of mechanical properties in both the neat clear cast and laminates are performed. Thermogravimetric analysis (TGA) data is presented to further examine thermal stability with weight loss as a function of temperature.

Table 1. Description of epoxy novolac vinyl esters (NVEs)tested in this report.

Resin	Description
F086	Commercial product, conventional NVE
XR 2227	Higher crosslink density NVE
XR 4140	Higher crosslink density NVE modified to retain good elongation
XR 4198	Highest crosslink density NVE, modified for pre- mium thermal resistance
NVE-4	Elastomer modified NVE, very high crosslink den- sity
NVE-5	Elastomer modified NVE, very high crosslink den- sity

2. EXPERIMENTATION

2.1 Materials

All resins tested in this report were epoxy novolac vinyl ester resins (NVE) prepared with proprietary methods and formulas by AOC, LLC. Metal salts were obtained from OMG, dimethyl aniline from Sigma-Aldrich, peroxides from AkzoNobel and United Initiators, and glass from Owens Corning. Grades of glass used were Owens Corning woven roving WR24/3010 (24.5 oz/yd2) and Owens Corning chopped strand mat M723 (1.5 oz/sf). Carbon fiber laminates were derived from Saertex USA unidirectional carbon fiber, 17yd2, oz/ Carbon 0/90.

2.2 Liquid Property Measurements

Viscosity measurements were performed on a Brookfield LV DV-II + viscometer. 340 g samples were contained in a 400 mL beaker, tempered and held at 25°C with viscosity measurements run for 60 seconds with an RV #2 spindle at 20 rpm. Gel times were performed on a Sunshine gel meter model 22-B using 100 g of catalyzed resin at 25 °C. Peak temperatures were captured using a Quick Disconnect RTD Omega thermocouple.

2.3 Clear Cast Preparation

Clear cast refers to the non-reinforced cured resin. Resin casts were prepared one of two methods, and these are specified in the results section. 400 g Of resin was initiated with either (1) 1% by weight Trigonox C tert-butyl peroxybenzoate (TBPB); or (2) 0.05% dimethylaniline, 0.15% of 12% Cobalt bis(2-ethylhexanoate) in mineral spirits, and 2% Trigonox K-90 cumene hydroperoxide (CHP). The initiated resins were poured between 12"x12" Mylar lined glass plates with 1/8" spacers. The samples were placed in an oven and ramped from 25 °C to 205 °C over the course of 30 hours. Resulting casts were cut and prepared into specimens for mechanical testing, thermogravimetric analysis and corrosion testing. In the section 3.3 Initiator and post cure studies, other peroxides were utilized and post cure schedules employed as detailed in that section.

2.4 Laminate Construction

ASME type II laminates were prepared using the F086 and the modified higher thermal performance MNVE candidates. The resins were formulated with 0.05% dimethylaniline, 0.15% of 12% Cobalt bis(2-ethylhexanoate) in mineral spirits, initiated with 2% Trigonox K-90 cumene hydroperoxide, and cured at room temperature. The laminates were all treated identically, made with seven layers of glass alternating between M723 chopped strand mat and WR24/3010 woven roving (C, W, C, W, C, W, C). The laminates were 44% glass by weight and 0.27" thick. After the laminates cured 16 hours at 25 °C, they were then post cured at 205 °C for 5 hours. Carbon fiber laminates were prepared with 6 plies of Saertex unidirectional carbon fiber. The plies were cut 16" x 20" and infused lengthwise (0" to 20"), the infusion was also transverse the fiber orientation cured at room temperature and had a carbon fiber percentage of 54% by weight.

2.5 Mechanical Testing

The laminates and clear cast specimens of the various resins were mechanically tested on an Instron series 5984 Universal Testing System via ASTM D638 (tensile) using a Epsilon Tech extensometer [3542-0200-025-HT2] and ASTM D790 (3-point flexural bend) using an Instron extensometer [2630-110]. Elevated temperature tests were conducted via these ASTM methods with an Instron Environmental chamber [3119-410] for property retention.

Tensile tests speeds were set to 0.20"/minute. Flexural test speeds and spans were set based on the thickness of the sample per ASTM D638. The clear casts were flexural tested at 0.05"/min with a 2.00" testing span. The glass laminates were flexural tested at 0.115"/min with a 4.40" testing span. The number of specimens tested per sample was at least five per ASTM D638.

Additional physical tests were conducted on the clear casts, such as ASTM D648 (Heat Distortion Temperature). ASTM D648 utilized a Dynisco HDV 3 (DTUL/VICAT) Tester equipped with Mahr Federal Maxum III displacement sensors. The Dynisco HDV 3 Tester's maximum operating temperature in air was 280°C due to its heat transfer medium. Dow 710R silicone fluid. Specimens were tested edgewise with a static flexural load of 264psi over a 3.94" span. The temperature of the tester was increased at 2°C/min until a 0.010" deflection was observed in the specimens. Thermocouples were used to report local temperatures once this deflection was observed.

2.6 Thermogravimetric Analysis

Powdered samples of clear casts, ranging from 6-8 mg, were scanned once from 25 °C to 700 °C at 20 °C per minute using a PerkinElmer TGA 7. A 20 ml/min nitrogen or air (as designated) purge gas flow was utilized. Each sample was tared to 100% weight and held for 5 minutes at 25 °C. One determination was made per sample and the thermal curve was reported. This Thermogravimetric Analysis test method falls roughly within the guidelines of ASTM E1131 for determining the thermal decomposition. These tests were also repeated with the TGA furnace exposed to air.

Limiting Oxygen Index Analysis

Clear castings were cut in dimensions of 3 or 4

inches by 10mm (+/- 0.25mm) with a 2 inch mark from the top. The castings limiting oxygen index (LOI) was measured using a Govmark Oxygen Index Module per ASTM D2863.

3. RESULTS

3.1 Liquid Properties

The NVE resins were tested according to standard liquid property tests for gel profile and viscosity as a first step to ensure their compatibility with traditional fabrication methods that are currently employed for UPR and VE composite applications. Table 2 lists liquid properties of today's technology and the higher heat resistant NVE candidates. Viscosities and gel times are in a normal range for conventional fabrication methods, and could be tailored with varying monomer content or inhibitor / promoter adjustments as needed.

Table 2.	Liquid p	properties	of conve	ntional NV	'E and	modified	NVEs
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Resin	Viscosity ¹ (cP)	Gel Time ² (min)	Total Time ² (min)	Peak Ex- otherm ² (ºC)	Specific Gravity ³
F086	400	25	40	199	1.08
XR 2227	460	26	39	210	1.09
XR 4140	220	24	32	206	1.08
XR 4198	300	19	25	196	1.09
XR 4501	400	20	24	213	1.20

1.Brookfield RV #2 spindle, 20 rpm at 25 $^\circ\text{C}$ 2.Gel time run at 25 $^\circ\text{C}$ with 100 g resin with 0.15% of 12% Cobalt bis (ethylhexanoate), 0.05% dimethyl aniline, and 2% Trigonox K-90 3. Specific gravity at 25 °C

3.2 Clear Cast Mechanical Properties

Premium mechanical properties are the hallmark of vinyl esters, and high heat resistance is a key characteristic for novolac vinyl esters. Thus, physical testing is required as a part of this study to evaluate higher thermal performance novolac vinyl esters. The validation of these candidates mechanically begins with testing non-reinforced clear cast specimens. Clear casts were prepared by curing the resins with 1% TBPB and post curing as outlined in the experimentation section. Tables 3 and 4 summarize flexural, HDT, and tensile properties, respectively. Higher HDT was achieved in all the candidates at the expense of strength and elongation.

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NVE-1 and NVE-2 achieve high flexural strength, with moderate tensile strength. Clear casts derived from NVE-3 exhibits HDT values that exceed the capability of the Dynisco HDV 3 tester at > 280 °C. NVE-1 and NVE-2 achieve high flexural strength, with moderate tensile strength. The FRNVE resin exhibits very good flexural strength, good modulus and an improved heat distortion temperature (200 °C) over today's commercially available fire retardant novolac vinyl ester (143 °C). This is achieved with increased crosslink density while still retaining flame retardant properties introduced by bromine bound to the polymer backbone.

Glass transition temperatures (Tg) were not able to be obtained by DMA (dynamic mechanical analysis) or DSC (differential scanning calorimetry). Specimens shattered in the DMA below their HDT without yet recording a Tg, and no thermal event resembling Tg was visible in the DSC either.

Table 3. Flexural (ASTM D790) properties at 25 °C and HDT (ASTM D648) of the 1/8" non- reinforced clear casts for the conventional NVE and modified NVEs engineered for higher thermal performance. Resins were cured with 1% TBPB and post cured according to schedule outlined in experimentation section.

Resin	Flexural Stre	ngth	Flexural f	HDT	
	psi	MPa	ksi	GPa	°C
F086	22,500	155	610	4.2	166
XR 2227	19,800	137	610	4.2	215
XR 4140	19,900	137	610	4.2	259
XR 4198	14,300	99	670	4.6	> 280
XR 4501	18,200	126	610	4.2	200

Table 4. Tensile properties (ASTM D638) at 25 °C of the 1/8" non-reinforced casts for the conventional NVE and modified NVEs engineered for higher thermal performance. Resins were cured with 1% TBPB and post cured according to schedule outlined in experimentation section.

Resin	Tensile Strength		Tensile I	Modulus	Tensile Elongation
	psi	MPa	ksi	GPa	%
F086	12,000	83	550	3.8	2.8
XR 2227	8,200	57	650	4.5	1.7
XR 4140	9,400	65	590	4.1	2.1
XR 4198	7,200	50	580	4.0	1.4
XR 4501	9,400	65	620	4.3	1.8

3.3 Initiator and Post Cure Studies

In general, the method to achieve the maximum heat distortion temperature in a composite or clear cast is to exceed the glass transition temperature of the matrix resin in the post cure while maximizing degree of cure. In all studies in this report, specimens were post cured to 205 °C, with the exception of this section. Lower post cure temperatures were investigated along with alternate peroxides in order to achieve maximum compatibility with methods used by fabricators today. Post curing to 205 °C may not be possible in some instances for fabricators, therefore room temperature gelling and lower post cure temperatures were pursued.

Utilizing the XR 4198 candidate for this study with 2% cumene hydroperoxide (Trigonox K-90) with 0.05% dimethyl aniline and 0.15% of 12% cobalt (bis ethylhexanoate) and gelling at room temperature, without any post cure, an HDT of only 85°C was obtained in the clear cast. However, the HDT, with only one hour at 120°C post cure, dramatically increases to > 280°C. It is possible the specimens continued to cure during the HDT measurement itself, but a minimum threshold of cure seems necessary via post cure to achieve a high HDT, as evidenced by the HDT of XR 4198 clear cast with 2.0% cumene hydroperoxide room temperature gel without post cure. Alternative catalysts also produced different results. XR 4198 clear cast made with 1.25% MEKP-925H, 0.15% of 12% cobalt (bis ethylhexanoate) and gelling at room temperature, a five hour post cure at 160 °C achieved an HDT of > 280 °C. Attempting to cure XR 4198 and the other

candidates with 98% benzoyl peroxide and heat resulted in crack clear casts despite gentle ramp rates.

3.4 Elevated Temperature Mechanical Properties

The target composite applications for these NVEs are in high temperature environments. While mechanical properties at room temperature (25°C) provide relative data to other existing technologies, and the HDT indicates these may be suitable at elevated temperature, elevated temperature mechanical testing is needed to validate these resins. Specimens for each NVE were mechanically tested as laminates. Clear casts were prepared as in section 2.3. Tensile and flexural properties, thus performance at elevated temperatures were measured as percent retention versus their tested values at 25°C (equation 1).

Equation 1

Percent Retention = [(Property value at X °C) x 100] / [Property value at 25 °C]

Vinyl ester resin is often combined with glass in most composite applications, and therefore glass reinforced laminate testing at elevated temperature is critical. Glass reinforced type II laminates, with alternating chopped strand mat and woven roving, were prepared as 44% glass and 0.27" thick. Specimens were cut for flexural and tensile tests and results are shown in Tables 5 and 6. Laminates were tested at 200 °C, far above the HDT of the F086. In these results, the marked improvement of the new NVEs over the F086 is most evident. Tensile properties are well maintained for XR 4198 the highest HDT candidate, while this candidate also performed best in the flexural testing.

Vinyl ester resin is sometimes combined with carbon fiber in the most demanding composite applications for improved strength and modulus. XR 4140 was chosen as a proof of concept for this testing due to its elongation. Likewise, these very demanding applications may involve high service temperatures that will continue to post cure the NVE laminate in service. XR 4140 carbon fiber laminates were tested at 25°C and at 200°C, with and without their traditional post cure of 205°C. These laminates were made with 6 layers of Saertex USA unidirectional carbon fiber to 54% carbon fiber by weight and 0.19" thickness. Specimens were cut for flexural and tensile tests and results are shown in Table 7. In these results, there is marked improvement over XR 4140 glass laminates in absolute values across the board. This improvement may arise from the use of carbon fiber and from the unidirectional nature of the reinforcement. Testing also revealed there were similar retentions for the modulus and flexural strength values between glass and carbon fiber on the post cured laminates. Tensile strength retention of the carbon Fiber XR 4140 laminate is thought to have been negatively impacted by the difficulty in testing and tabbing high modulus unidirectional composites, especially at elevated temperature as failures occurred on grip surfaces. The mechanical testing also revealed that the primary difference between post curing verse not post curing these carbon fiber XR 4140 laminates was better strength retention in exchange for less strength at room temperature.

3.5 Thermogravimetric Analysis

While the retention of mechanical properties at elevated temperatures improved in all candidates, weight loss is another factor that deserves consideration when qualifying a material for service at high temperature. Thermogravimetric analysis (TGA) was performed on non-reinforced clear cast candidates, as well as the commercially available product. These were parts of the same casts prepared for testing in section 3.2. TGA requires a small sample, usually milligram quantities, that is heated and mass is recorded. In the case of all resins tested, less than 3% is lost by 350 °C, followed rapid decomposition occurs at about 400 °C. Additional testing will be performed with larger cast and laminate samples heated under air in an oven held at elevated temperatures.



Figure 2. Therogravimetric analysis (TGA) of the novolac vinyl ester resins under nitrogen.

Table 5.	Flexural properties	(ASTM D790)	of type II	laminates	derived	from	conventional	NVE	and
modified	NVE's engineered fo	r higher therm	al perform	nance at 25	5°C and	200	°C.		

	F	lexural Streng	ţth	F	lexural Modu	llus
Resin	25 °C psi MPa	200 °C psi MPa	Percent Reten- tion	25 °C ksi GPa	200 °C ksi GPa	Percent Re- tention
F086	34,400 237	5,200 36	15	1,470 10.1	530 3.7	36
XR 2227	34,600 239	14,700 101	43	1,540 10.6	1,220 8.4	79
XR 4140	38,700 267	17,500 121	45	1,610 11.1	1,180 8.1	73
XR 4198	31,000 214	16,300 112	53	1,370 9.4	1,250 8.6	91

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	Flex	kural Strength	ı	Fle	exural Modulu	lus		
Resin	25 °C psi MPa	200 °C psi MPa	Percent Retention	25 °C ksi GPa	200 °C ksi GPa	Percent Retention		
F086	24,700 170	9,300 64	38	1,990 13.7	1,010 7.0	51		
XR 2227	25,200 174	16,800 116	67	2,130 14.7	1,730 11.9	81		
XR 4140	24,300 168	16,600 114	68	2,120 14.7	1,690 11.7	80		
XR 4198	19,400 134	16,000 110	83	1,930 13.3	1,770 12.2	92		

Table 6. Tensile properties (ASTM D638) of type II laminates derived from conventional NVE and modified NVE's engineered for higher thermal performance at 25 °C and 200 °C.

 Table 7. Tensile and flexural properties of the infused carbon fiber reinforced laminate derived from XR 4140.

	Flex	kural Strengtl	'n	Fle	xural Modulu	IS
Infused Carbon Fiber Laminate	25 °C psi MPa	200 °C psi MPa	Percent Retention	25 °C ksi GPa	200 °C ksi GPa	Percent Retention
No post cure	94,200 649	28,200 194	30	11,200 77	6,000 41	53
Post cured at 200 °C	72,600 500	33,700 232	46	10,800 75	5,500 38	51
	Ter	nsile Strength	ı	Те	nsile Modulu	S
	25 °C psi MPa	200 °C psi MPa	Percent Retention	25 °C ksi GPa	200 °C ksi GPa	Percent Retention
No post cure	94,000 648	34,800 121	37	13,300 92	11,100 76	83
Post cured at 200 °C	76,400 527	32,100 240	42	13,400 92	11,000 76	82



Figure 3. Therogravimetric analysis (TGA) of the novolac vinyl ester resins under air.

3.6 Limiting Oxygen Index (LOI) Testing: XR 4501

Comparison of today's premium commercially available fire retardant novolac vinyl ester and the higher heat resistant analog (XR 4501) was performed by limiting oxygen index testing. The output in this test defines the minimum oxygen content required to support combustion of the material. The reference material serving as a comparison to the XR 4501 was a premium commercially available novolac vinyl ester meeting ASTM E84 Class 1 flame spread. The higher heat resistant XR 4501 outperformed the commercial novolac flame retardant vinyl ester, with 33% oxygen required to support combustion compared to 29% required for the commercial FR novolac vinyl ester. Both resins contained the identical concentration of bromine. This result is due largely to the superior heat resistance of the XR 4501 exhibiting an HDT of 200 °C compared to the commercial fire retardant novolac product at 143 °C. Further standardized testing of the XR 4501 with flame spread and smoke tests (i.e. ASTM E84 and others) will be required prior to use flame retardant applications.

4. CONCLUSIONS

Modified epoxy novolac vinyl ester resins designed for premium thermal performance were characterized and presented. Liquid properties of these candidates indicated that the resins would be compatible with traditional fabrication methods used for unsaturated polyester and vinyl ester resin composite production. Viscosity and gel time may require further tailoring for specific applications, but these minor modifications would not have an effect on the validation tests presented in this study. Corrosion properties of these candidates will need to be investigated further depending on the composite application. All candidates demonstrated improved elevated mechanical properties compared to the commercially available novolac vinyl ester in both in laminates and clear cast testing. Initial results for the higher HDT fire retardant novolac vinyl ester were presented. The improved limited oxygen index results and much higher HDT could prove useful in composites for fire retardant safety equipment. Thus far, applications utilizing these candidates have included chimney liners, composite tooling, composite pipes, and high temperature electrical applications, all of which are in trial phases.

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