

Technical Paper

New High Temperature Resistant Vinyl Ester

Abstract

There has been a need for a high temperature resistant vinyl ester for pipes to carry hot gases, for reinforcement in dual laminates and for applications such as quench vessels. A new high temperature resistant vinyl ester has been developed with a heat distortion temperature of 330°F (165°C). Liquid resin properties, cast mechanical properties, laminate mechanical properties, hardness development and some initial corrosion resistant properties of this new vinyl ester resin will be provided.

Introduction

Options for the development of high heat resistant resins are polyesters and vinyl esters. Since vinyl esters have inherently better impact resistance than polyesters, a high temperature resistant novolac vinyl ester was developed. Engineers often need mechanical properties on castings and on ASME RTP-1 laminates. High temperature tensile properties of both the casting and the ASME RTP-1 laminate were tested and the results will be presented. High temperature tensile properties were obtained because tensile modulus values are required by engineers to design fiberglass equipment for high temperature applications. Corrosion test results in toluene and methanol at 100°F (37.8°C) as well as resistance to 350°F (176.7°C) air were obtained. Comparisons will be made to standard novolac resins. Results of bisphenol vinyl esters will also be included since they are the most common vinyl esters sold. The new high temperature novolac resin will be referred to as Vipel® F086. The standard novolac resin will be called Vipel® F085. A standard bisphenol A epoxy vinyl ester will be called Vipel® F010.

Experimental

Certain key requirements were imposed.

- Styrene content must be =35%
- Resin cast heat distortion must be >325°F (162.8°C)
- Vipel® F086 resin should cure similar to Vipel® F085 and Vipel® F010

-The Vipel F086 high temperature resistance of cast and ASME RTP-1 laminate should be higher than that of Vipel F010 and Vipel F085.

-The corrosion resistance of Vipel F086 to toluene and methanol at 100°F (37.8°C) plus air at 350°F (176.7°C) air must equal or exceed that of Vipel F010 and Vipel F085.

Test Procedure

Several polymers made with novolac epoxy resins were prepared using the standard system of end capping the polymer with methacrylic acid. Liquid properties including viscosity, gel, styrene contents, Barcol Hardness development, etc. were tested with standard equipment and methods that are typically used in the industry. The cast preparation is found in figure 1. ASME RTP-1 and ASTM C 581 laminates were post cured following the post cure schedule of the castings. ASME RTP-1 laminates were made with one layer of veil, three plies of 1.5 ounce per square foot mat (450 grams per square meter), one ply of 24 ounce per square yard (814 grams per square meter) woven roving, one layer of mat, one layer of woven roving and finally one ply of mat. ASTM C 581 coupons were made with 3 plies of 1.5 ounce per square foot (450 grams per square meter) chopped strand mat with one layer of C glass veil on each side. Flexural strength and flexural modulus was tested on the control laminates. The laminates were then placed in toluene and methanol at 100°F (37.8°C) for 1, 3, and 6 months. After each of these time periods, the laminates were removed from the oven, allowed to stabilize at ambient temperature and then were tested. Likewise, coupons were placed in a 350°F (176.7°C) oven and removed at 1, 3, 6 and 9 months. They were allowed to return to ambient temperature and then were tested. Secondary bonding was simply tested by prying two laminates apart. Resins were promoted with 0.3% cobalt 6%, 0.05% N,N-dimethylaniline and catalyzed with 2.0% cumyl hydroperoxide. Vipel F010, Vipel F085 and Vipel F086 resins were used to prepare laminates with 3 plies of 1.5 ounce chopped strand mat that were 3.5 inches (8.6 cm) by 8 (20.3 cm) inches. After 5 days a strip of Mylar, one inch wide, was placed on the 3.5 (8.6 cm) inch end of each of these laminates. Another laminate was applied over each of the original laminates and allowed to cure for 3 days. Then a wedge was used to pry the laminates apart starting a plastic release film.

Results

- Vipel F086® that contains 35% styrene was produced. See figure 2.
- The heat distortion of Vipel F086 is 330°F (165.6).
- The laminate cure rate of Vipel F086 is similar to that of Vipel F085 and somewhat faster than Vipel F010. See figure 3.

Cast and ASME RTP-1 laminates high temperature tensile properties of Vipel F086, Vipel F085 and Vipel F010 were obtained and are shown on figure 5, 6, 7 and 8. Vipel® F086 retained more mechanical strength at high temperatures than Vipel F085 and Vipel F010. The high temperature tensile properties retention of a laminate is much greater than that of a casting. Thus the glass reinforcement has a significant effect on this property.

- The glass contents of Vipel F086, Vipel F085 and Vipel F010 laminates were 36-40%.
- Vipel F086 and Vipel F085 have similar resistance to methanol and toluene after 6 months. Based on Barcol Hardness values, both Vipel F086 and Vipel F085 have better resistance to methanol and toluene than Vipel F010, as expected. See figures 9, 10, 11, 12, 13 and 14.
- ASTM C 581 laminates of Vipel F086, Vipel F085 and Vipel F010 were exposed to 350°F (176.7°C) air for 9 months. See figure 7 and 8. Flexural strength, flexural modulus, Barcol Hardness were all similar. Both Vipel F085 and Vipel F086 retained more weight than did the Vipel F010. See figures 15, 16 and 17.
- All laminates bonded well in this test.

Discussion

A standard cumyl hydroperoxide which is also known as cumene hydroperoxide (CHP) catalyst is suggested for novolacs since they are quite reactive. One advantage to using CHP over MEKP catalysts is that foaming is not an issue. Even though a good secondary bond was obtained, there have been a number of reported instances of delamination when the surface of a novolac laminate was not ground before applying the secondary laminate. Thus it would be prudent to sand the surface with a 16-24 grit grinding pad before applying a second laminate. Like Vipel F085 resins, the Vipel F086 is not recommended for caustic environments. Vipel F010 resins can be used in caustic environments.

Applications

Vipel F086 is suited to reinforce thermoplastic liners in dual laminate applications where high heat resistance is needed. Vipel F086 is also suited for hot chemical environments such as carrying hot gases or for quench vessels when extra assurance is needed over the marginal heat resistant and corrosion resistant offered by Vipel F085.

Conclusions

- Vipel F086 has a styrene content of 35% and a heat distortion temperature of 330°F (165.6°C).
- The Vipel F086 viscosity, gel and cure properties are typical of Vipel F085 and Vipel F010 resins; thus, there are no fabrication issues.
- High temperature cast and laminate tensile properties of Vipel F086 are significantly higher than that of either Vipel F085 or Vipel F010.
- Both Vipel F086 and Vipel F085 are more resistant to methanol and toluene than Vipel F010.
- At the 9 month interval, Vipel F086 and Vipel F085 have lost less weight at 350°F (176.7°C) than Vipel F010.

Future Developments

- Twelve month 350°F (176.7°C) air exposure testing will be completed.
- Nine and twelve month corrosion resistance of Vipel F086, Vipel F085 and Vipel F010 will be compared.

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Figure 1

CASTING PREPARATION

CATALYST AND CURE SCHEDULE	QUANTITY AND TIME
Catalyst system	
Benzoyl Peroxide (BPO), %	1.0
Cure schedule	
160°F (60°C), hours	4
200°F (93°C), hours	1
240°F (116°C), hours	1
280°F (138°C), hours	1
320°F (160°C), hours	2

Figure 2

RESIN LIQUID PROPERTIES

PROPERTY	Vipel® F010	Vipel® F085	Vipel® F086
77°F (25°C) Brookfield viscosity, spindle #2 @ 20 rpm, cps	400	440	400
Styrene content, %	39	33	35
Gel time with 0.3% cobalt 6, 0.05% DMA and 2.0% CHP (90% active), minutes	31	22	24
Gel to peak exotherm, minutes	16	11	15
Peak exotherm, °F(°C)	347 (175)	384 (195.6)	390 (198.9)
Specific gravity	1.06	1.08	1.08

Figure 3

COMPOSITE CURE RATE

DETAILS	Vipel® F010	Vipel® F085	Vipel® F086
Laminate preparation			
Promoters:			
Cobalt (6%),%	0.3	0.3	0.3
DMA, %	0.05	0.05	0.05
Catalyst			
CHP content on the resin, %	2.0	1.25	1.25
Construction			
Plies of 1.5 oz per square foot (450 grams per square meter) chopped strand mat	3	3	3
Glass content, %	30	30	30
Cure progression			
Gel time, minutes	35	25	26
Time to tack free after gel, minutes	125	100	90
Shore D Hardness after 2 hours after gel	35	45	55
Barcol Hardness (934) after 24 hours	15	20	25
Barcol Hardness (934) after 72 hours	35	40	40

Figure 4

CAST MECHANICAL PROPERTIES at 25°C

PROPERTY	Vipel® F010	Vipel® F085	Vipel® F086
Tensile strength, psi (MPa)	12,800(88)	11,200(77)	10,000(69)
Tensile modulus, psi (GPa)	460,000(3.2)	540,000(3.7)	550,000(3.8)
Elongation, %	6.2	3.3	2.4
Flexural strength, psi (MPa)	22,000(153)	21,500(148)	16,800(116)
Flexural modulus, psi (GPa)	500,000(3.5)	540,000(3.7)	620,000(4.3)
Heat distortion temperature, °F (°C)	248 (120)	300 (148.9)	330(165.6)
Barcol Hardness (934)	40	44	41
Specific gravity	1.14	1.15	1.16

Figure 5

CAST TENSILE STRENGTH WITH INCREASING TEMPERATURE

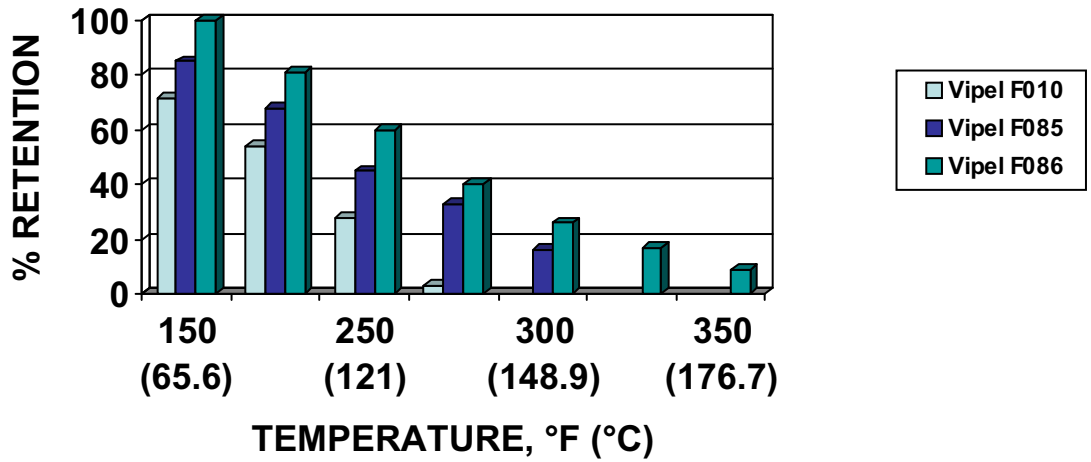


Figure 6

CAST TENSILE MODULUS WITH INCREASING TEMPERATURE

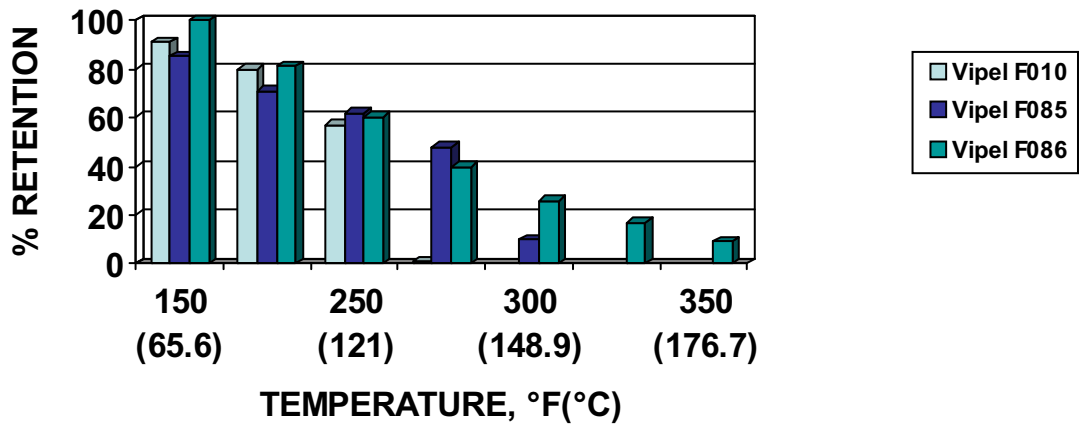


Figure 7

ASME RTP-1 LAMINATE TENSILE STRENGTH WITH INCREASING TEMPERATURE

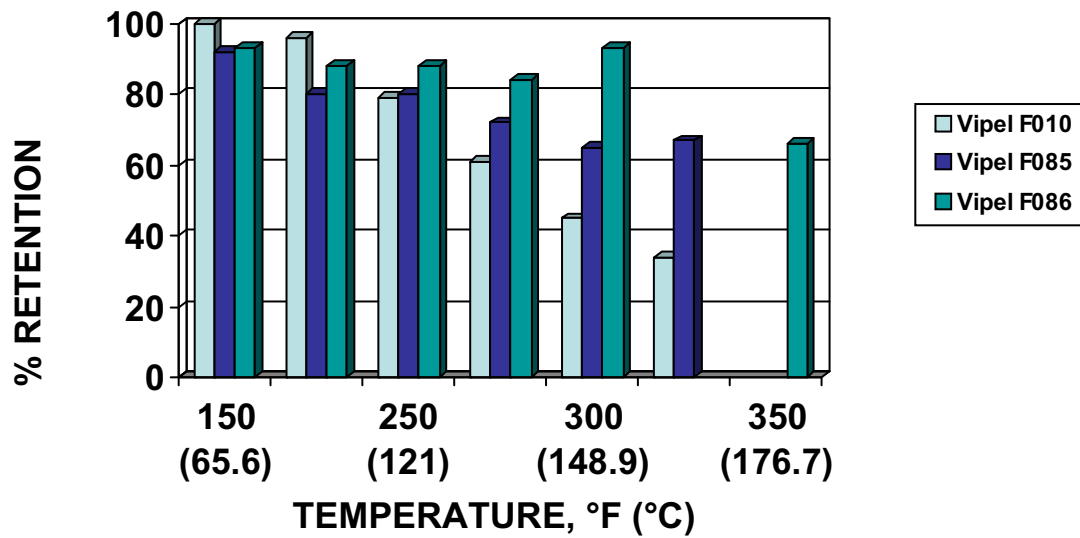


Figure 8

ASME RTP-1 LAMINATE TENSILE MODULUS WITH INCREASING TEMPERATURE

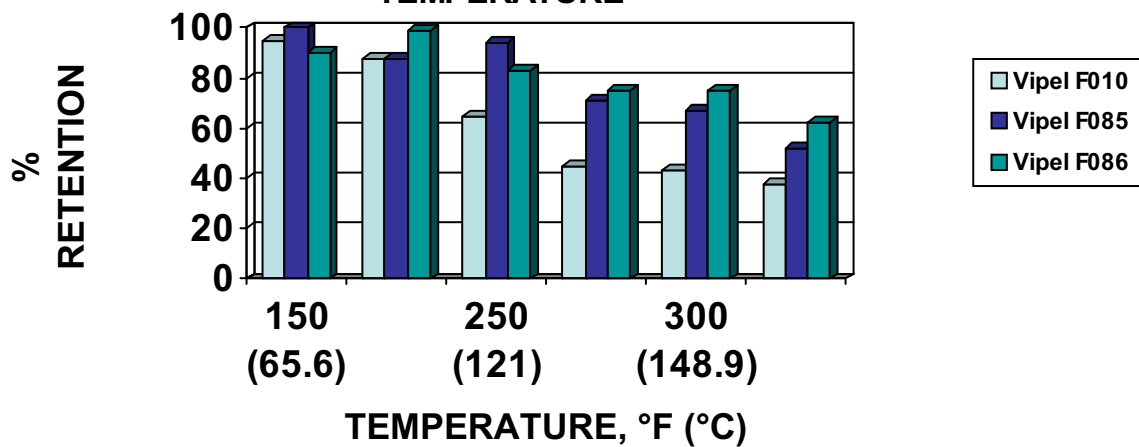


Figure 9

ASTM C 581 LAMINATES MADE WITH Vipel® F086 AND EXPOSED TO TOLUENE AT 100°F (37.8°C)

	Properties	Initial	1 Month	3 Months	6 Months
1.	Flexural Strength, psi (MPa)	23,300 (161)	23,000 (159)	24,600 (170)	25,200 (174)
	% Retention		99	106	108
2.	Flexural Modulus, psi (GPa)	1,120,000 (7.72)	1,090,000 (75.1)	1,080,000 (74.5)	1,190,000 (82.1)
	% Retention		97	96	106
3.	Barcol Hardness 934	52	58.8	61	50
	% Retention		113	117	96
4.	Weight (g) - original		58.222	58.294	60.317
	Weight (g) - exposed		58.263	58.357	60.408
	% weight change		0.07	0.11	0.15

Figure 10

ASTM C 581 LAMINATES MADE WITH Vipel® F085 AND EXPOSED TO TOLUENE AT 100°F (37.8°C)

	Properties	Initial	1 Month	3 Months	6 Months
1.	Flexural Strength, psi (MPa)	23,200 (160)	24,300 (168)	25,600 (177)	21,400 (148)
	% Retention		105	110	92
2.	Flexural Modulus, psi (GPa)	1,050,000 (72.4)	1,120,000 (77.2)	1,160,000 (80)	1,090,000 (75.2)
	% Retention		107	110	104
3.	Barcol Hardness 934	51	58	61	50
	% Retention		114	120	98
4.	Weight (g) - original		56.377	55.459	60.354
	Weight (g) - exposed		56.401	55.496	60.421
	% weight change		0.04	0.07	0.11

Figure 11

ASTM C 581 LAMINATES MADE WITH Vipel® F010 AND EXPOSED TO TOLUENE AT 100°F (37.8°C)

	Properties	Initial	1 Month	3 Months	6 Months
1.	Flexural Strength, psi (MPa)	29,900 (206)	35,400 (236)	30,200 (208)	20,600 (142)
	% Retention		118	101	69
2.	Flexural Modulus, psi (GPa)	1,210,000 (83.4)	1,120,000 (77.2)	870,000 (60)	680,000 (46.9)
	% Retention		93	72	56
3.	Barcol Hardness 934	45	43	32	0
	% Retention		94	71	0
4.	Weight (g) - original		46.306	53.393	49.619
	Weight (g) - exposed		47.18	55.188	53.128
	% weight change		1.89	3.36	7.07

Figure 12

ASTM C 581 LAMINATES MADE WITH Vipel® F086 AND EXPOSED TO METHANOL AT 100°F (37.8°C)

	Properties	Initial	1 Month	3 Months	6 Months
1.	Flexural Strength, psi (MPa)	23,300 (161)	24,600 (170)	28,200 (194)	19,900 (137)
	% Retention		106	121	85
2.	Flexural Modulus, psi (GPa)	1,120,000 (82.7)	880,000 (60.7)	930,000 (64.1)	720,000 (49.6)
	% Retention		79	83	64
3.	Barcol Hardness 934	52	33	32	22
	% Retention		64	62	42
4.	Weight (g) - original		57.743	58.851	57.013
	Weight (g) - exposed		59.875	62.227	61.767
	% weight change		3.69	5.74	8.34

Figure 13

ASTM C 581 LAMINATES MADE WITH Vipel F085 AND EXPOSED TO METHANOL AT 100°F (37.8°C)

	Properties	Initial	1 Month	3 Months	6 Months
1.	Flexural Strength, psi (MPa)	23,200 (160)	24,600 (170)	19,700 (136)	18,600 (128)
	% Retention		106	85	80
2.	Flexural Modulus, psi (GPa)	1,050,000 (72.4)	780,000 (53.8)	720,000 (49.6)	750,000 (51.7)
	% Retention		74	69	71
3.	Barcol Hardness 934	51	32	28	18
	% Retention		63	55	35
4.	Weight (g) - original		56.333	57.848	57.375
	Weight (g) - exposed		58.4	61.346	61.714
	% weight change		3.67	6.05	7.56

Figure 14

Vipel F010 ASTM C 581 LAMINATES MADE WITH Vipel® F010 AND EXPOSED TO METHANOL AT 100°F (37.8°C)

	Properties	Initial	1 Month	3 Months	6 Months
1.	Flexural Strength, psi (MPa)	29,900 (206)	20,400 (141)	18,500 (128)	20,100 (139)
	% Retention		68	62	67
2.	Flexural Modulus, psi (GPa)	1,210,000 (83.4)	790,000 (54.5)	650,000 (44.8)	750,000 (51.7)
	% Retention		65	54	62
3.	Barcol Hardness 934	45	14	0	0
	% Retention		32	0	0
4.	Weight (g) - original		48.454	47.997	48.065
	Weight (g) - exposed		52.365	52.502	52.259
	% weight change		8.07	9.39	8.73

Figure 15

STM C 581 LAMINATES MADE WITH Vipel® F086 AND EXPOSED TO 350°F (176.7°C) AND TESTED AT AMBIENT TEMPERATURE

	Properties	Initial	1 Month	3 Months	6 Months	9 Months
1.	Flexural Strength, psi (MPa)	23,300 (161)	26,400 (182)	23,900 (165)	28,100 (194)	26,200 (181)
	% Retention		113	103	121	112
2.	Flexural Modulus, psi (GPa)	1,120,000 (77.2)	1,120,000 (77.2)	1,140,000 (78.6)	1,300,000 (89.6)	1,030,000 (71.0)
	% Retention		100	102	116	92
3.	Barcol Hardness 934	52	62	61	65	62
	% Retention		119	118	126	120
4.	Weight (g) - original		58.34	58.27	57.64	56.86
	Weight (g) - exposed		58.01	57.52	56.4	55.34
	% weight change		-0.56	-1.29	-2.15	-2.68

Figure 16

ASTM C 581 LAMINATES MADE WITH Vipel F085® AND EXPOSED TO 350°F (176.7°C) AND TESTED AT AMBIENT TEMPERATURE

	Properties	Initial	1 Month	3 Months	6 Months	9 Months
1.	Flexural Strength, psi (MPa)	23,200 (160)	23,400 (161)	21,500 (148)	26,100 (180)	23,000 (159)
	% Retention		100	93	113	99
2.	Flexural Modulus, psi (GPa)	1,100,000 (75.8)	1,030,000 (71.0)	980,000 (67.6)	1,120,000 (77.2)	910,000 (62.7)
	% Retention		98	93	107	87
3.	Barcol Hardness 934	51	58	57	60	62
	% Retention		113	112	118	122
4.	Weight (g) - original		59.83	58.76	59.82	58.72
	Weight (g) - exposed		59.47	57.95	58.47	57.06
	% weight change		-0.6	-1.4	-2.3	-2.82

Figure 17

ASTM C 581 LAMINATES MADE WITH Vipel® F010 AND EXPOSED TO 350°F (176.7°C) AND TESTED AT AMBIENT TEMPERATURE

	Properties	Initial	1 Month	3 Months	6 Months	9 Months
1.	Flexural Strength, psi (MPa)	29,900 (206)	26,000 (69.0)	29,600 (204)	32,900 (227)	36,500 (252)
	% Retention		87	99	110	122
2.	Flexural Modulus, psi (GPa)	1,210,000 (83.4)	1,130,000 (77.9)	1,200,000 (82.7)	1,380,000 (95.2)	1,330,000 (88.5)
	% Retention		93	99	114	110
3.	Barcol Hardness 934	45	59	61	63	61
	% Retention		131	135	140	136
4.	Weight (g) - original		46.152	48.701	49.801	49.07
	Weight (g) - exposed		45.121	47.009	47.465	46.39
	% weight change		-2.23	-3.47	-4.69	-5.46