

Technical Paper

Characteristics of Vinyl Ester Laminates Suitable for Chimney Liner Applications after High Temperature Thermal Stress

Introduction

Chimney liner fiberglass laminates made from vinyl ester resins need to survive brief high temperature excursions during non-typical plant operations. A test vehicle was developed to characterize laminate performance based on differences in appearance, mechanical, and thermal properties before and after a thermal excursion. High performance vinyl ester resins perform exceptionally well in these tests as they exhibit high levels of property retention.

Background

In the 1970's, government regulation of stack emissions from coal-fired units led to the deployment of flue gas scrubber systems. The changing nature of the flue gas as a result of these scrubber systems would require a corrosion resistant liner in the chimneys due to the condensation of corrosive chemicals. Recently, more stringent requirements have led to new scrubber technologies and have expanded the use fiberglass reinforced plastics (FRP) in chimney liners and gas ducts due to their properties, ease of fabrication, and cost.

The ASTM Standard D 5364 "Standard Guide for Design, Fabrication, and Erection of Fiberglass Reinforced Plastic Chimney Liners with Coal-Fired Units" cites four specific operating temperature environments and two abnormal temperature environments for a chimney liner constructed out of FRP, Tables 1 & 2.

It is the objective of this paper to characterize the performance of a composite constructed of a high performance vinyl ester resin after a simulated thermal stress in excess of the most severe environment (440°F / 227°C flue gas temperature) recited in the ASTM standard. No attempt is made to determine if a chimney liner would survive the thermal stress due to the many unique variables for each application (static and dynamic loads,

etc.). Rather, it is the focus of this paper to measure the change in material performance after a brief high temperature thermal stress.

Vinyl Ester Resins

Two specific high performance vinyl ester resins were utilized for the testing. These resins were selected based on their application history, ability to meet the requirements of ASTM D 5364, and excellent high temperature performance.

The ASTM D 5364 standard specifies minimum flame resistance and corrosion resistance requirements. Two different vinyl ester resins were identified that meet these requirements without the addition of a flame retardant synergist, (antimony compound, etc.). A brominated bisphenol A epoxy vinyl ester (BBVE) resin and a brominated epoxy novolac vinyl ester (BNVE) resin were chosen. Both of these resins are commercially available.

Both resins are manufactured through traditional methods well known through out the industry. Typically, the epoxy component is charged into a reaction vessel with a stoichiometric amount of methacrylic acid, heated until the epoxy-acid reaction is complete, and dissolved in styrene monomer. The specific formulations used are representative of the commercially available products and contain added styrene, air release agent, promoters, and storage stabilizers.

High Temperature Chimney Liner Testing

Simulated chimney liner laminates were fabricated with embedded thermocouples and exposed to a high temperature thermal stress on the corrosion barrier. The intent was to simulate a non-typical plant condition where flue gas temperatures approach 550 °F (288 °C) for 30 minutes. Temperatures of the corrosion barrier, structural

laminates, and backside of the structural laminates were measured during the test. The appearance of the laminates was evaluated after the thermal stress to investigate laminate integrity and determine if the corrosion barrier was breached.

The reinforcement schedule was chosen to represent that of a typical chimney liner and is represented in Figure 1. In this study D155 (15 oz/yd² unidirectional) glass was used to represent the hoop windings due to its similar weight and thickness.

One laminate was fabricated with each vinyl ester resin. The resins were catalyzed with 1.25% methyl ethyl ketone peroxide (MEKP) and post-cured for four hours at 176°F (80°C).

A test laminate with the embedded thermocouples was attached to the opening of an industrial grade muffle furnace at room temperature. The furnace was started with an attached data acquisition device recording temperatures 10 times per second. One thermocouple was placed inside the furnace within 1 inch of the face of the test laminate to record the furnace air temperature. After 30 minutes at 500 - 600°F (260°C - 315°C), the test was stopped and the specimen was allowed to cool. A thermal profile of the actual temperatures recorded during one of the chimney liner laminates thermal tests is in Figure 2.

Unidirectional Fiberglass Laminate Testing

Laminates were prepared from each high performance vinyl ester and two plies of unidirectional fiberglass oriented in the same direction. The weight and grade of unidirectional fiberglass was chosen to be indicative of the 15 ounce/yd² unidirectional tape used in the construction of a typical chimney liner laminate. This unidirectional tape is oriented in the axial direction to carry the static loads of the chimney liner can while in service.

The resins were catalyzed with 1.25% MEKP and post-cured for four hours at 176°F (80°C). Half of each laminate was baked at 500°F (260°C) in a forced-air convection oven for 30 minutes.

Samples of each laminate with the unidirectional at 0° and 90° were tested for tensile properties per ASTM D 3039 "Standard Test Method for the Tensile Properties of Polymer Matrix Composite Materials". Specimens of each laminate were tabbed with 0.059" of epoxy glass-fiber composite laminates to reduce stress at the clamps during tensile testing. The tabs were adhered to the laminates with a commercially available two component adhesive and post-cured for 4 hours at 122°F (50°C) prior to tensile testing. A total of five specimens of each sample were tested. Some data was excluded from further analysis for tab slippage during testing.

Instrumental Analysis

Samples of each vinyl ester prepared from thin clear castings were evaluated for thermal degradation characteristics by Thermal Gravimetric Analysis per ASTM D 3850. In this method, a small sample of the polymer is heated in air until 5% weight loss is achieved. The polymer is characterized by the temperature at which 5% weight loss occurs and the onset temperature at which significant weight loss begins. An additional scan was performed on each thin clear casting where the temperature profile is indicative of the 30 minute 500°F (260°C) bake used on the laminates for mechanical testing. In this case, the polymers were characterized by total weight loss.

Samples of each vinyl ester prepared from thin clear castings were evaluated for thermal performance by Dynamic Mechanical Analysis per ASTM D 4065 and ASTM E 1640. In this method, a small sample of cast resin is subjected to a dynamic force in the three-point bending configuration while the temperature is slowly increased. The polymer is characterized by the onset temperature associated with the loss of the storage modulus, the peak tan delta temperature, and the percent storage modulus retained above glass transition temperature. The glass transition temperature can be obtained alternately from the onset of the storage modulus loss (ASTM E 1640) or the peak of the tan delta curve (ASTM D 4065).

Samples of each laminate prepared for tensile property testing were also tested for changes in thermal performance before and after the 500°F (260°C) bake by Dynamic Mechanical Analysis. These samples were also characterized by glass transition temperature (T_g) and percent retained storage modulus above T_g.

Results

Both resins experienced some discoloration during the high temperature chimney liner thermal stress tests as indicated by the before and after photographs (Figure 3 and Figure 4). Some delamination was evident around the embedded thermocouples, but it was localized and did not breach the corrosion barrier. The subsurface blisters are due to air entrapment around the thermocouple wires, large differences in thermal expansion between the wires and the laminate, and micro-voids around glass fibers formed during hand lamination. Trim pieces of the same laminates without thermocouples exhibited significantly less blisters when exposed to the same thermal stress profiles, (Figure 5). Clearly, the importance of void-free laminates in high temperature applications can not be overstated.

Characterizing these resins by Dynamic Mechanical Analysis (DMA) revealed thermo-mechanical differences between the two resins, Table 3. As expected, the brominated epoxy novolac vinyl ester (BNVE) exhibited a 30% higher glass transition temperature.

The glass transition temperature (T_g) is a fundamental property of thermosetting resins. This temperature represents the point above which the resin reversibly transitions from a glassy solid to a rubbery semi-solid. While T_g can be measured by many different methods with each reporting a slightly different value, these values were derived from the peak of the tan delta curve from the DMA, (Figure 6).

The heat distortion temperatures (HDT) for these resins obtained by ASTM D 648 correlate precisely to the glass transition temperature data obtained by DMA, Table 4.

The heat distortion temperature can be approximated from the average of the glass transition temperature and the onset of the glass transition temperature obtained from the storage modulus and tan delta curves (Figure 6).

Comparing the two vinyl esters by Thermal Gravimetric Analysis found similar thermal stability performance, Table 5. The degradation onset temperature is the temperature at which significant degradation begins. Significant degradation is associated with the breakage of chemical bonds in the polymer and the associated formation of char and liberation of smoke. While the resins exhibited remarkably different glass transition temperatures, they degrade at roughly the same temperature. These degradation temperatures are all above the representative temperatures chosen to test a given abnormal event in a chimney liner.

Unidirectional fiberglass laminates prepared with two plies of 15 ounce/yd² of unidirectional glass fiber of each vinyl ester were evaluated by Dynamic Mechanical Analysis before and after a bake at 500°F (260°C) for 30 minutes. While both resins did exhibit some discoloration at these temperatures (Figure 7), they did not degrade as evident by the following data comparison in Table 6.

Any significant degradation would be accompanied by a reduction in glass transition temperature associated with the breakage of chemical bonds in the polymer. Samples of clear cast films of the resins were also evaluated for weight loss by Thermal Gravimetric Analysis after a 500°F (260°C) 30 minute bake. Only minimal weight loss was detected and probably due to the loss of free material present in the resin, catalyst, and formulation additives as represented in Table 7.

Tensile properties of unidirectional laminates from each vinyl ester were compared at 0° and 90° before and after a 30 minute 500°F (260°C) bake in a forced air convection oven in Table 8. For comparison purposes, the glass contents and average thicknesses for the laminates are reported in Table 9. With a 0° fiber orientation, both vinyl esters retained nearly all of their tensile strength and modulus considering some tab slippage and resultant partial failures occurred on the baked samples. This is as

expected with the glass fiber carrying the predominate load. Tensile strength values in the 90° orientation were nearly 90% of the original value for both vinyl esters. However, the value of this data is subject to scrutiny due to the uncertainty inherent to testing unidi-rectional laminates at 90°.

Tensile elongation values were measured on the unidirectional laminates but not considered for comparison due to the nature of the failure (periodic filament bundle failure during test) and the difficulties associated with measuring displacement with highly oriented reinforced plastics (sudden displacement during testing affecting the extensometer).

Conclusions

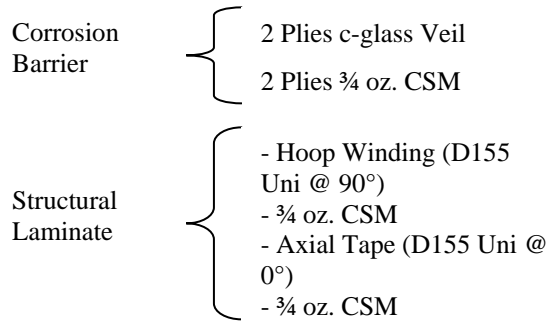
The high temperature testing of simulated chimney liner laminates demonstrates that resins can survive brief thermal excursions well above their Tg or heat distortion temperature without significant property degradation. Laminates fabricated from brominated bisphenol A epoxy vinyl ester or brominated epoxy novolac vinyl ester resins experienced only minor discoloration and weight loss after a high temperature thermal stress. Chimney liner and gas duct applications for these resins can now benefit from demonstrated thermal stability to brief high temperature thermal stress.

Acknowledgement

We would like to acknowledge the support and assistance of Winston J. Renoud, P.E., President of Fiberglass Structural Engineering, for his valuable advice in developing the experimental design for this study.

Author

As a Corrosion Specialist for AOC LLC, Scott has 20 years of experience in developing thermosetting resins for corrosion, fire resistance, and other demanding applications. He has a BA Degree in Chemistry from the University of Pittsburgh, 9 US patents for high performance resins and composites, and is a member of the ACMA, ACS, and IPC.



Note: the structural laminate reinforcement sequence is repeated approximately 8X until a 0.5" thick laminate is achieved

Figure – 1

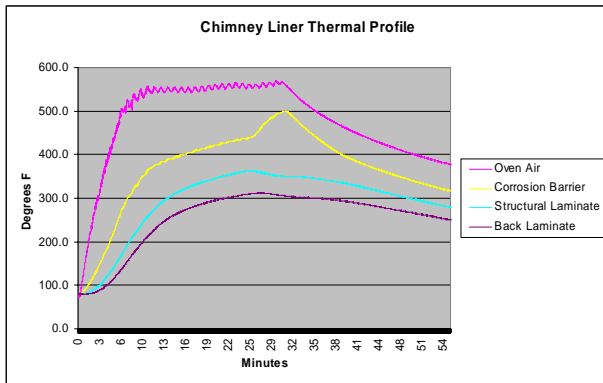
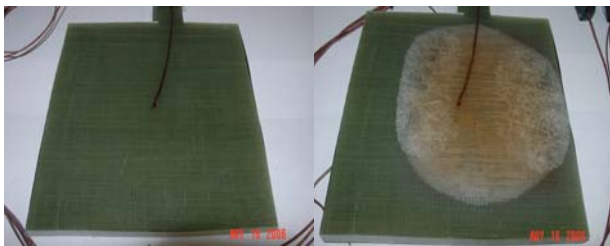
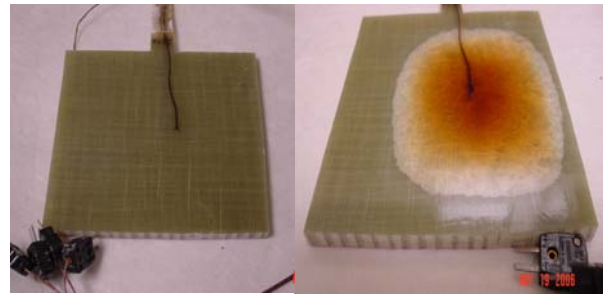


Figure – 2



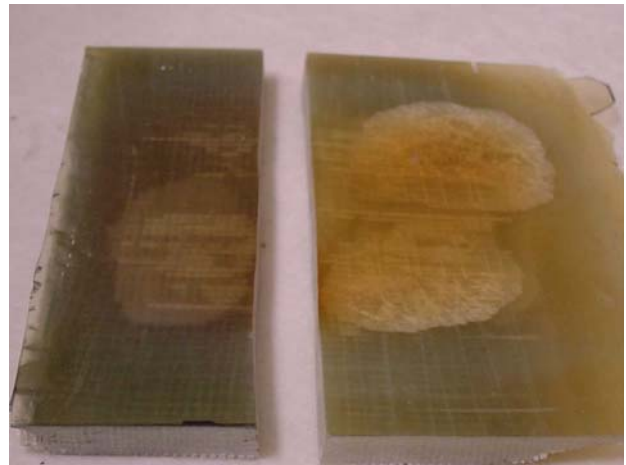
Brominated Bisphenol A Epoxy Vinyl Ester (BBVE)
Before After Thermal Stress

Figure – 3



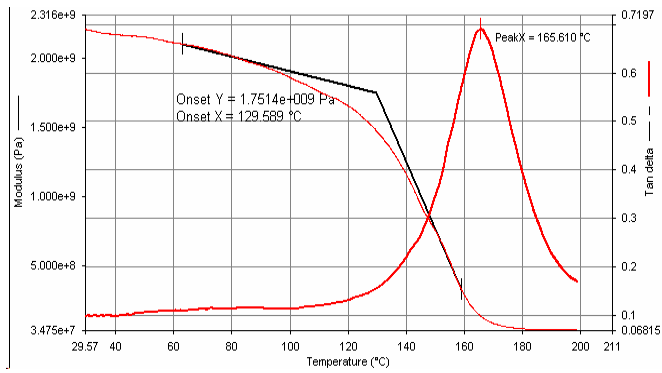
Brominated Epoxy
Novolac Vinyl Ester (BNVE)
Before After Thermal Stress

Figure - 4



Brominated Epoxy VE Brominated Epoxy Novolac VE
Both after Thermal Stress w/o Thermocouples

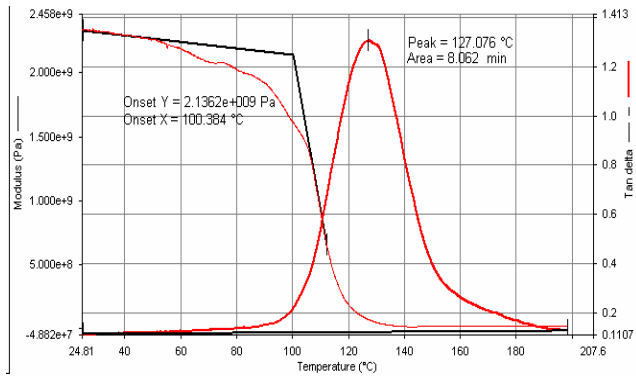
Figure – 5



Brominated Epoxy Novolac VE DMA Scan



After Bake Before
Brominated Epoxy VE



Brominated Epoxy VE DMA Scan



After Bake Before
Brominated Epoxy Novolac VE

Figure - 6

Figure - 7

Operating Environment and Flue Gas Temperature

Condition 1	Saturated flue gas	60°C
Condition 2	Condensation Occurring	60 - 93°C
Condition 3	No Condensation	60 - 93°C
Condition 4	No Scrubber System	60 - 93°C

Table - 1

Abnormal Environments and Flue Gas Temperature

Condition 1	Flue Gas cooled with quench	121°C Max
Condition 2		227°C Max

Table - 2

DMA Data

	Tg (°C)	Tg Onset (°C)	Modulus Above Tg
BBVE	127.1	100.4	2.04%
BNVE	165.6	129.6	1.59%

Table - 3

Heat Distortion vs Glass Transition Temperature

	Tg (°C)	Actual HDT (°C)	Tg Onset (°C)	Average Tg & Tg Onset
BBVE	127.1	112	100.4	114
BNVE	165.6	143	129.6	148

Table - 4

TGA Data

	Degradation Onset (°C)	5% Wt Loss temp (°C)
BBVE	360	365
BNVE	350	353

Table - 5

Laminate Change after Bake

	Change After 30 min 260°C Bake	
	ΔTg (°C)	Δ Tg Onset (°C)
BBVE	+7.9	+6.0
BNVE	+13.4	+13.4

Table - 6

Laminate Change after Bake

	Weight Loss After 30 min 260°C Bake
BBVE	3.53%
BNVE	2.03%

Table - 7

Unidirectional Laminates - 90° Fiber Orientation

	Condition	Strength (Mpa)	Modulus (Gpa)	Elongation (%)
BBVE	AR	16.4	8.2	0.21
	Bake	14.1	7.6	0.19
BNVE	AR	18.7	11	0.17
	Bake	17.2	N/A	N/A

AR = As-received before bake

N/A = Data omitted for displacement sensor error

Unidirectional Laminates - 0° Fiber Orientation

	Condition	Strength (Mpa)	Modulus (Gpa)	Elongation (%)
BBVE	AR	758	32	2.45
	Bake	765	42	2.55
BNVE	AR	862	41	2.66
	Bake	779	40	2.66

Table - 8

Unidirectional Laminate Characteristics

	Glass Content	Thickness (mils)
BBVE 90°	45.7%	48
BNVE 90°	55.5%	36
BBVE 0°	57.5%	42
BNVE 0°	62.1%	37

Table - 9