High Temperature Resistant Brominated Novolac VE

COMPOSITES 2013
American Composites Manufacturers Association January 29-31, 2013
Orlando, Florida USA

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ABSTRACT

A novel brominated novolac vinyl ester has been recently commercialized. This resin has a unique combination of high heat distortion, excellent corrosion performance, and remarkable fire resistance. The properties of a composite made from this resin are presented along with a comparison to other resins.

RESIN TECHNOLOGY

Novolac vinyl esters resin, as the name implies, are produced from novolac epoxies rather than bisphenol-A epoxies like more traditional vinyl ester resins. The novolac epoxy contributes increased functionality to the resin which yields a higher cross-link density. The higher cross-link density results in a higher heat distortion temperature (HDT) and in most cases, improved chemical resistance.

Analogous to this differentiation, is that brominated novolac epoxy-based vinyl esters are also produced from novolac epoxies rather than bisphenol-A epoxies. Brominated novolac vinyl esters also have, in most cases, improved chemical resistance over the brominated bisphenol-A vinyl ester resins. However, the heat distortion temperature of a brominated novolac vinyl ester was significantly less than a novolac vinyl ester without bromine.

The improvement in the HDT was not the same in brominated resins when switching the epoxy from bisphenol-A to novolac. This disparity is displayed in Table 1.

Also, commercially available brominated novolac vinyl ester resins require an Antimony synergist to achieve a flame spread rating of 25 or less by ASTM E84 “Standard Test Method for Surface Burning Characteristics of Building Materials”. A flame spread of 25 or less is of-ten specified for fire resistance. However, equipment owners and inspectors desire a translucent composite for inspection which can only be provided without any add-ed fillers or Antimony.

TEST METHODOLOGY

A clear casting of the new brominated novolac epoxy-based vinyl ester (NBNVE) resin was prepared with 1% benzoyl peroxide and post- cured at 160°C for 5 hours. The casting was evaluated for tensile properties via ASTM D638, flexural properties via ASTM D790, heat distortion temperature (HDT) via ASTM D648 Method A, and hardness via ASTM D2583.

Clear castings of the NBNVE resin were prepared with different catalyst combinations and post-cured at different times and temperatures to investigate the affect to heat distortion temperature via ASTM D648 Method A.

Laminates of the NBNVE resin were prepared per ASTM C581 and baked in a forced-air convection oven at 177°C (350ºF) for one year. Samples of the laminate were tested for flexural properties, hardness, and weight change after one, three, six, nine, and twelve months.

A 24 foot panel (in 3 of 8’ sections) was prepared to obtain a flame spread and smoke developed rating per ASTM E84 testing with NBNVE resin and 2-plies of 2oz/sf chopped-strand mat at ~30% glass by weight. The panels were post-cured at 100°C for 3 hours.

RESULTS AND DISCUSSION

In Table 2, the cast mechanical properties of the new resin (NBNVE) are compared to another commercially available brominated novolac vinyl ester (BNVE) resin. The NBNVE has improved flexural and tensile strength over the current BNVE resin. The heat distortion temperature (HDT) of the NBNVE is 24°C higher than the BNVE indicating improved heat resistance. Unlike the other brominated novolac vinyl ester (BNVE) resin, this HDT is consistent with other novolac resins that do not contain bromine.

The affect to post cure profile and catalyst type is characterized in Table 3. The HDT benefits from a higher temperature secondary catalyst (TBPB) and longer post cure times at high temperatures. In high temperature applications, the NBNVE resin may post cure in service.

Laminates of the NBNVE resin have excellent property retention after one year at 177°C as shown in Graph 4. This temperature is well above the resin HDT and indicative of the novolac epoxy backbone.

The fire performance characteristics of composites made from brominated novolac vinyl ester resins are shown in Table 5.

Without the addition of any Antimony Oxide or other fillers, the flame spread rating and smoke developed index warrant a Class 1 or A rating in the NBNVE. This is superior to a composite made from BNVE which requires 3% Antimony Trioxide to achieve the same flame spread classification.

CONCLUSIONS

A new brominated novolac epoxy-based vinyl ester resin was created with improved properties. This resin has a higher heat distortion temperature and improved fire performance over other avail- able brominated novolac epoxy-based vinyl ester resins.

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Table 1: Vinyl Ester Resin Heat Distortion

Epoxy Chemistry	Halogen	Heat Distortion Temperature	” HDT
Bisphenol-A	No Bromine	105°-120°	0.5°
	Brominated	106°-116°	
Novolac	No Bromine	150°-180°	-44°
	Brominated	121°	

Table 2: Mechanical Properties of Brominated Novolac Epoxy-based Vinyl Ester Resins

Property	Test Method	Units	NBNVE	BNVE
Flexural Strength	ASTM D790	psi	22,400	19,000
Flexural Modulus	ASTM D790	Kpsi	600	530
Tensile Strength	ASTM D638	psi	14,400	10,500
Tensile Modulus	ASTM D638	Kpsi	670	500
Tensile Elongation (Break)	ASTM D638	%	3.5	3 - 4
Heat Distortion	ASTM D648	°C	145	121
Hardness	ASTM D2583	Hard Barcol	46	40

Table 3: Heat Distortion vs. Catalyst Type and Post Cure Profile

Post Cure Temperature	Post Cure Time	1.25% MEKP	1.25% MEKP 0.2% TBPB	1.0% BPO	1.0% BPO 0.2% TBPB
138°C	2 hours	N/A	N/A	138°C	N/A
149°C	5 hours	142°C	145°C	151°C	147°C
160°C	4 hours	147°C	147°C	150°C	150°C

MEKP = methylethylketone peroxide
TBPB = t-butyl perbenzoate
BPO = 98% benzoyl peroxide
N/A = Not Available

Graph 4: Property Retention After Oven Bake at 177°C

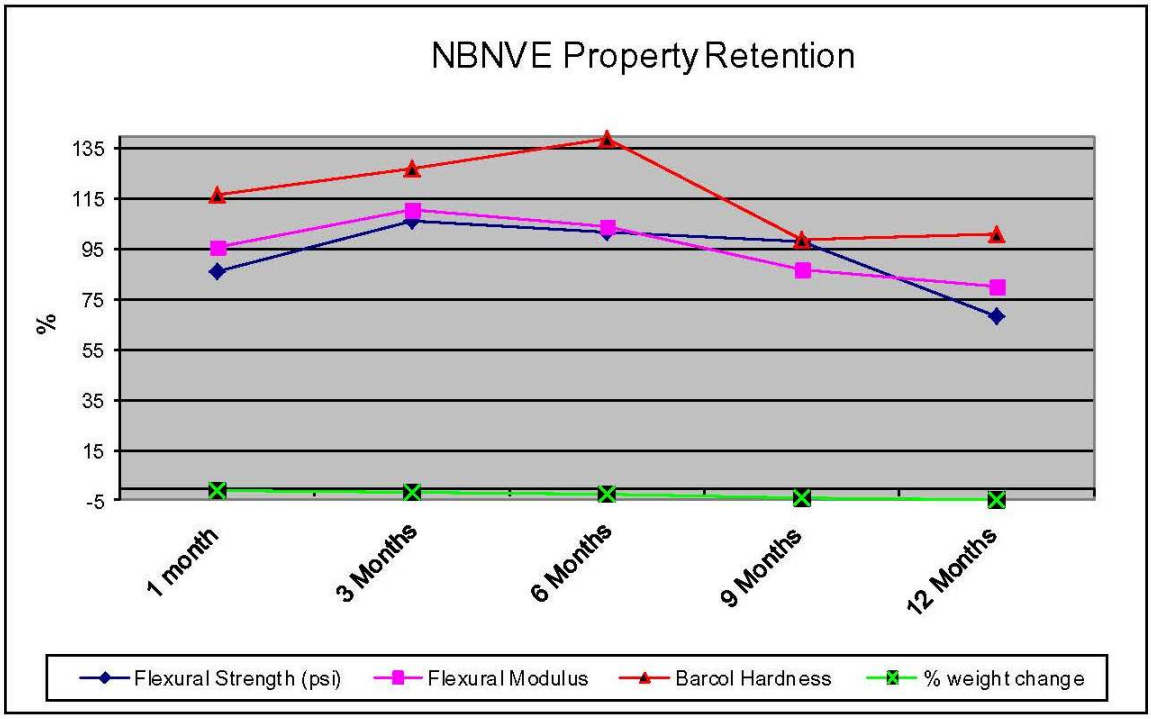

Table 5: Surface Burning Characteristics of Brominated Novolac Epoxy-based Vinyl Ester Resin Composites

Resin	Antimony Trioxide	Flame Spread Rating	Smoke Developed Index
NBNVE	0%	25	300
BNVE	3%	d25	N/A

Test Method = ASTM E84
NBNVE Laminate = 2-plies of 2oz/sf CSM @ ~30% glass & Post Cured 100°C for 3 hours