CVC Thermoset Specialties	Technical Service Report	RLP090713

Hypro™ Reactive Liquid Polymer Toughened Vinyl Ester Composites
Suitable for Wind Turbine Blades

Summary:

Functional butadiene copolymers known as Hypro RLP (reactive liquid polymers) are known to increase toughness of several thermoset resins as epoxies and vinyl esters. Specifically, CTBN (carboxyl terminated butadiene-acrylonitrile) and its associated epoxy resin adducts are used as tougheners for epoxy adhesives featuring extraordinary peel strength. These same CTBN liquid polymers are being used in matrix resins for carbon fiber and glass reinforced composites. One class of unique resins is elastomer modified vinyl esters. This document reviews some of those systems and work underway aimed at further developing the technology in applications as wind blade composites.

Results- Neat Resins

The unique resins referred to are CTBN elastomer modified bisphenol A epoxy derived vinyl esters known as Derakane 8084 or similar materials. A material property increased by the addition of a Hypro CTBN to vinyl esters is fracture toughness quantified by the expression G_{Ic} equating to the energy necessary to initiate and propagate a crack in the resin. Data in Table I illustrate the concept of enhanced G_{Ic} through the inclusion of CTBN in Derakane 8084. Compared to an unmodified vinyl ester as Derakane 411-45, 8084 is 200% tougher based on a G_{Ic} criterion.

Table I- Elastomer and Unmodified Vinyl Ester Resins

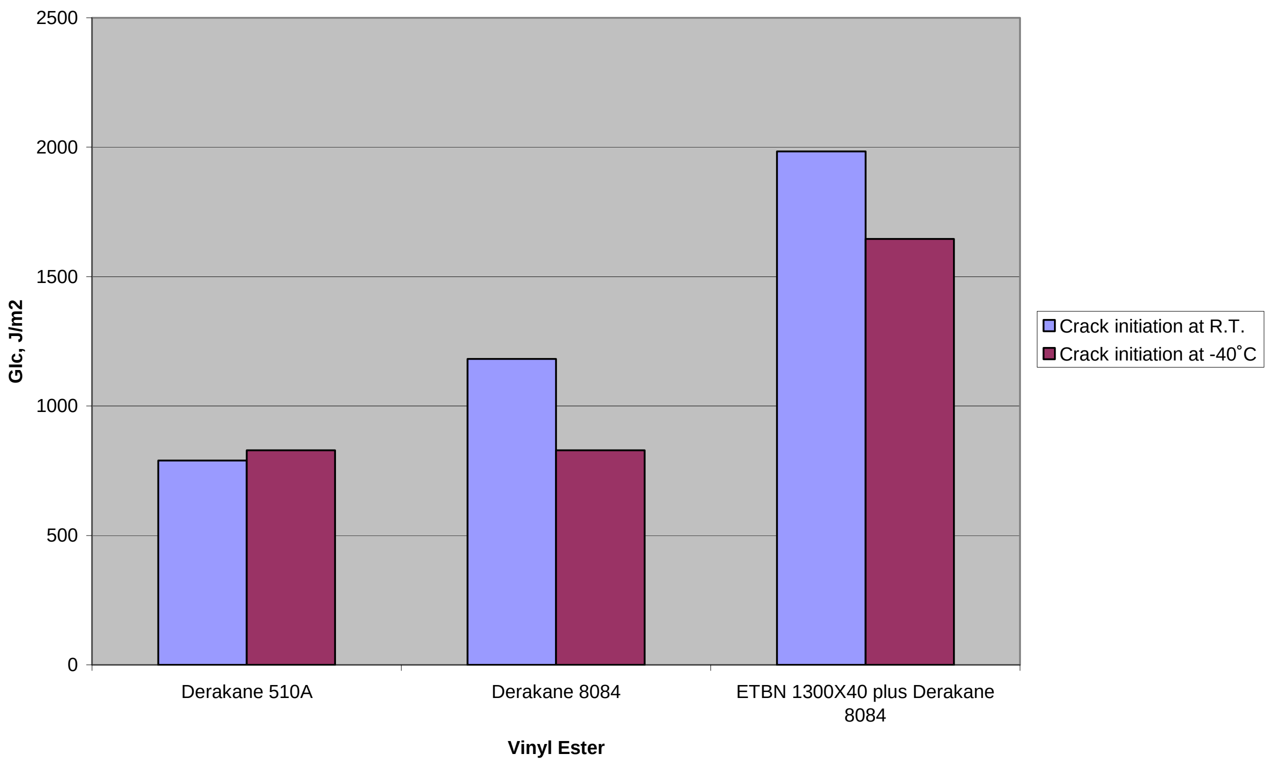
Recipe No.	1	2
Derakane 411-45, g	100	-
Derakane 8084, g	-	100
MEK peroxide *, g	2	2
Cobalt naphthenate**, g	0.5	0.5
Tensile strength, MPa	42	64
Tensile elongation, %	1.19	5.64
Tensile modulus, GPa	3.29	2.54
K_{Ic}, $MN/m^{3/2}$	0.627	0.981
G_{Ic}, J/m^2	105	335
Tg, ˚C (DSC)	120	113

*9% active O_2
** 6%
(K_{Ic} is another fracture mechanics term denoting toughness).

Results: Composites

Derakane 8084 in a glass reinforced composite is appreciably more crack resistant than an unmodified vinyl ester resin. Figure I provides fracture toughness data comparing it to a brominated vinyl ester in the form of Derakane 510A in a E-glass reinforced composite. Also data are included based on additional rubber modification of Derakane 8084 that will be explained in more detail in Further Work section of this document. Crack initiation was determined at room temperature and low temperature (-40˚C).

Figure I-Interlaminar Fracture Toughness for Glass Reinfoced Vinyl Ester Composites



The wind blade composite area has generated a considerable amount of fatigue data comparing epoxy, unsaturated polyester and vinyl ester matrix resins. Figure 18 taken from a paper presented at an American Institute of Aeronautics and Astronautics conference cites greater fatigue resistance of a Derakane 8084-glass composite than those based on either a UPE (unsaturated polyester) or an unmodified vinyl ester (reported as VE-1). VE-2 is Derakane 8084.

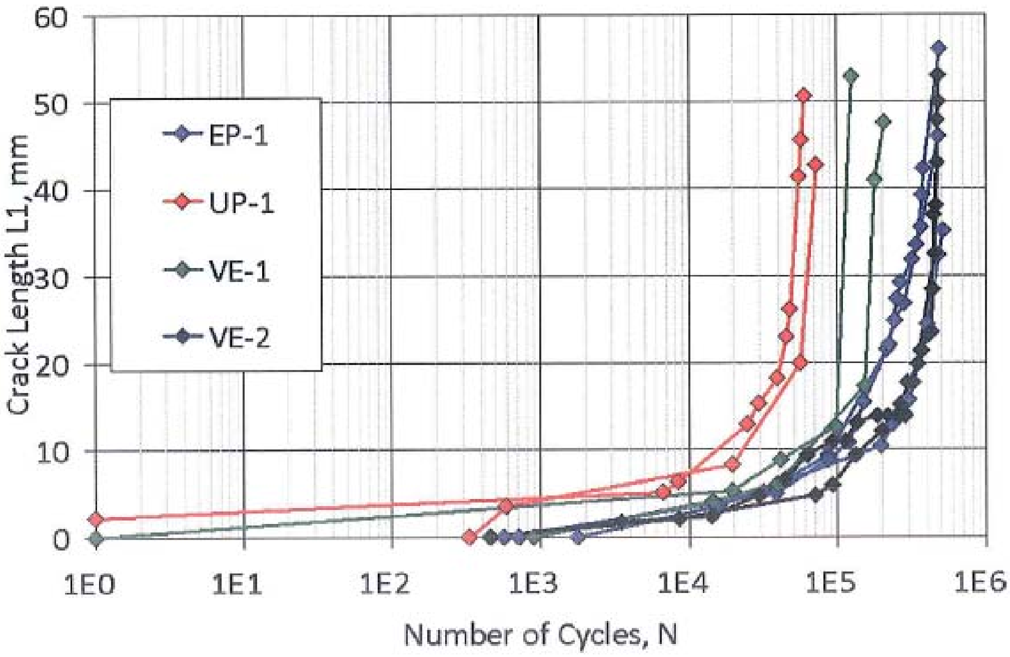


Figure 18. Delamination Growth in Fatigue for Various Resins, Complex Coupon with Two Plies Dropped, Maximum Load 44.5 kN, R = 0.1.

Further Work:

Elastomer modified vinyl esters as 8084 can be toughened more so by addition of ETBN 1300X40, a styrene diluted epoxy functional butadiene-acrylonitrile copolymer. For instance, G_{Ic} can be increased to greater than 2000 J/m^2 with a small amount of ETBN 13000X40 added to Derakane 8084. As such ETBN 1300X40/Derakane 8084 systems are being evaluated in industrial and wind blade composites.