CVC Thermoset Specialties
An Emerald Performance Materials Company

Fracture Toughness of Elastomer Modified, E-glass Reinforced Vinyl Ester Composites

Scope:

Introduction to elastomer modified, glass reinforced vinyl ester composites was made at SAMPE Fall Technical Conference in 2007 in the form of a paper, Elastomer Toughened Vinyl Esters. The concept of phase separated rubber in a continuous phase of glassy, thermoset resin was described by way of several examples of CTBN (carboxyl terminated butadiene-acrylonitrile) modified epoxies and vinyl esters. Additionally, toughness was quantified by a fracture mechanics term known as critical strain-energy release rate identified as G_c.

Inclusion of CTBN reactive liquid polymers and derivatized versions thereof are particularly effective as tougheners for epoxy and vinyl ester resins. The vast majority of work associated with such toughened compositions has been in adhesives or bulk specimens. However the cited paper provides composite fracture toughness data determined by using the Double Cantilever Beam (DCB) methodology. Those data featured an elastomer modified vinyl ester represented by Derakane 8084.

Beyond that further modification of the resin was achieved by adding a reactive liquid polymer referred to as ETBN 1300X40. The polymeric portion of 1300X40 is an epoxy/CTBN reaction product using 2 moles of liquid DGEBA (diglycidyl ether of bisphenol A) to 1 mole of CTBN 1300X8 (17% acrylonitrile content). It also contains styrene monomer at 50% by weight.

Additional Mode I interlaminar fracture toughness information has been developed complementing those found in the SAMPE paper to be presented in this write-up.

Results:

The glass previously used was an unidirectional E-glass fabric (15.5 oz. /yd.^{2}) while this study used an unidirectional E-glass fabric (24 oz. /yd.^{2}). Importantly, low temperature performance was determined by testing DCB specimens at -40˚C noting that only room temperature data were reported earlier.

Figure 1 contains crack initiation values for Derakane 8084 and ETBN 1300X40 modified Derakane 8084 (recipe was 10.7 parts of ETBN 1300X40 to 100 parts of Derakane 8084). Clearly, the inclusion of additional ETBN elastomer enhances crack initiation at room and low temperatures. There was a 30% reduction in fracture toughness for Derakane 8084 from room temperature to -40˚C whereas there was a 17% reduction in the same property for the ETBN/Derakane 8084 composition.

Figure 1-Interlaminar Fracture Toughness

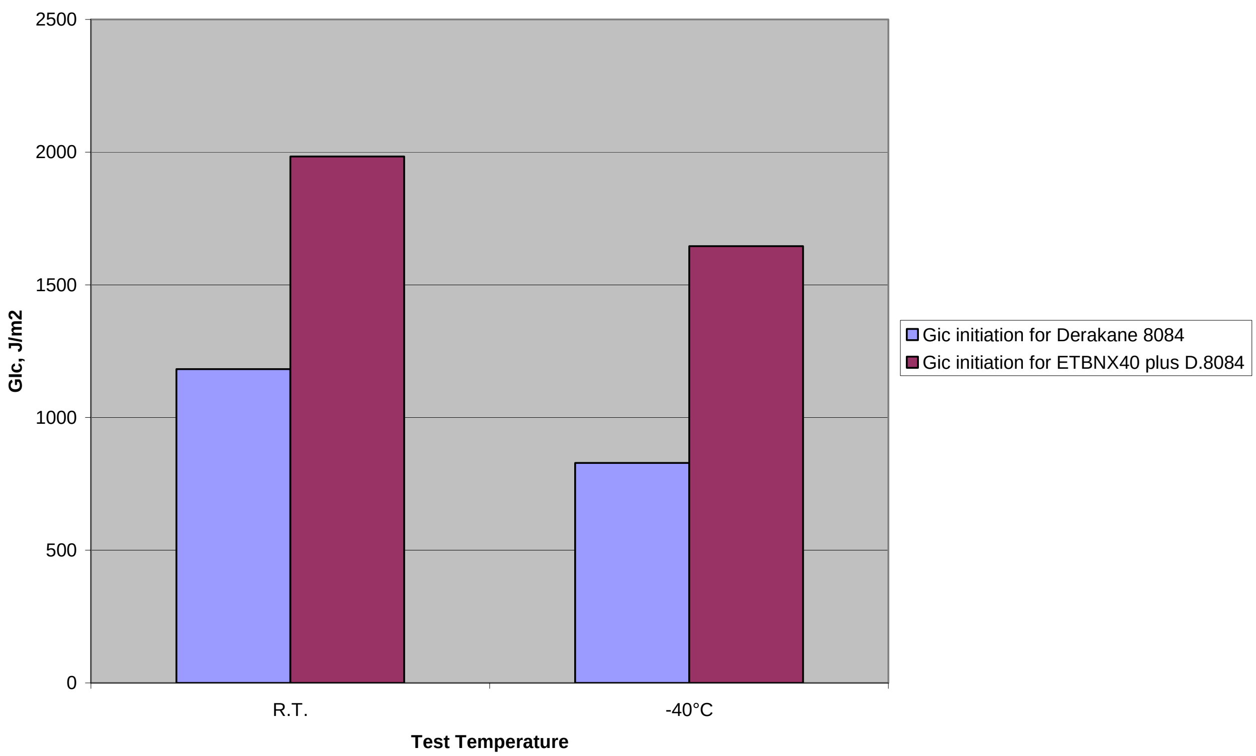

Figure 2 contains crack propagation values for Derakane 8084 and ETBN 1300X40 modified Derakane 8084. There was approximately a 25% reduction in crack propagation value for Derakane 8084 from room temperature to -40˚C while essentially there was no decrease in crack propagation for the ETBN 1300X40 modified Derakane 8084 traversing the same temperature range.

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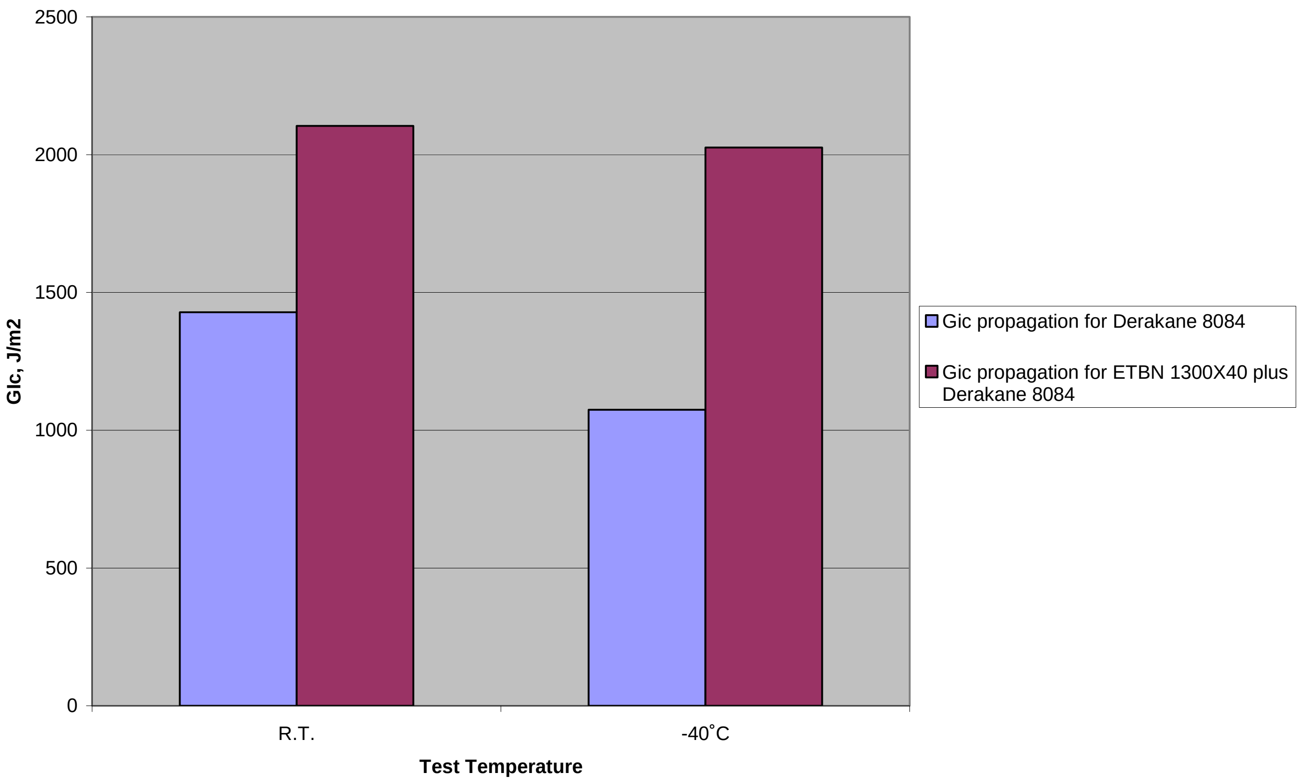
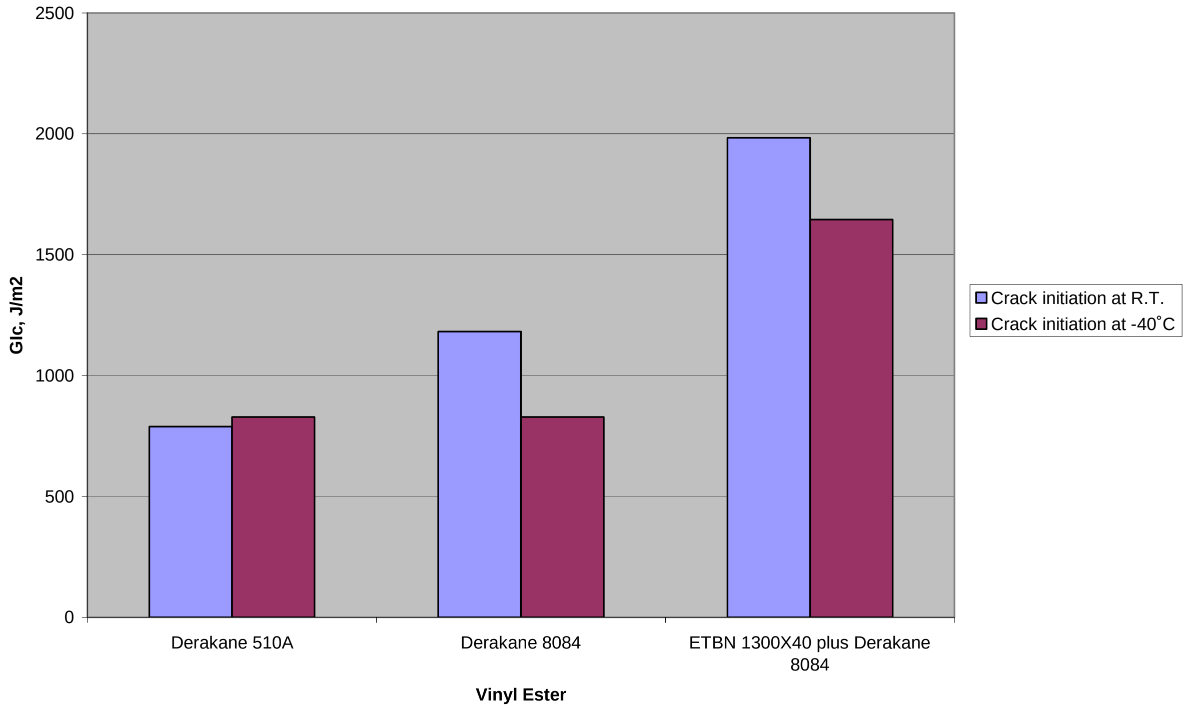
Figure 2- Interlaminar Fracture Toughness



A resin often used in composites for its flame resistance properties is Derakane 510A, a brominated vinyl ester. Interlaminar fracture toughness for a vacuum infused E-glass reinforced Derakane 510A composite was reported in an internal memo by Center for Composite Materials-University of Delaware. Crack initiation and propagation were determined at room temperature and low temperature similarly to the aforementioned data based on Derakane 8084 and ETBN 1300X40 modified Derakane 8084. Initiation and propagation values may be found in Figure's 3 and 4 respectively noting that the contents of Figure's 1 and 2 are included for comparative purposes.

Figure 3- Interlaminar Fracture Toughness



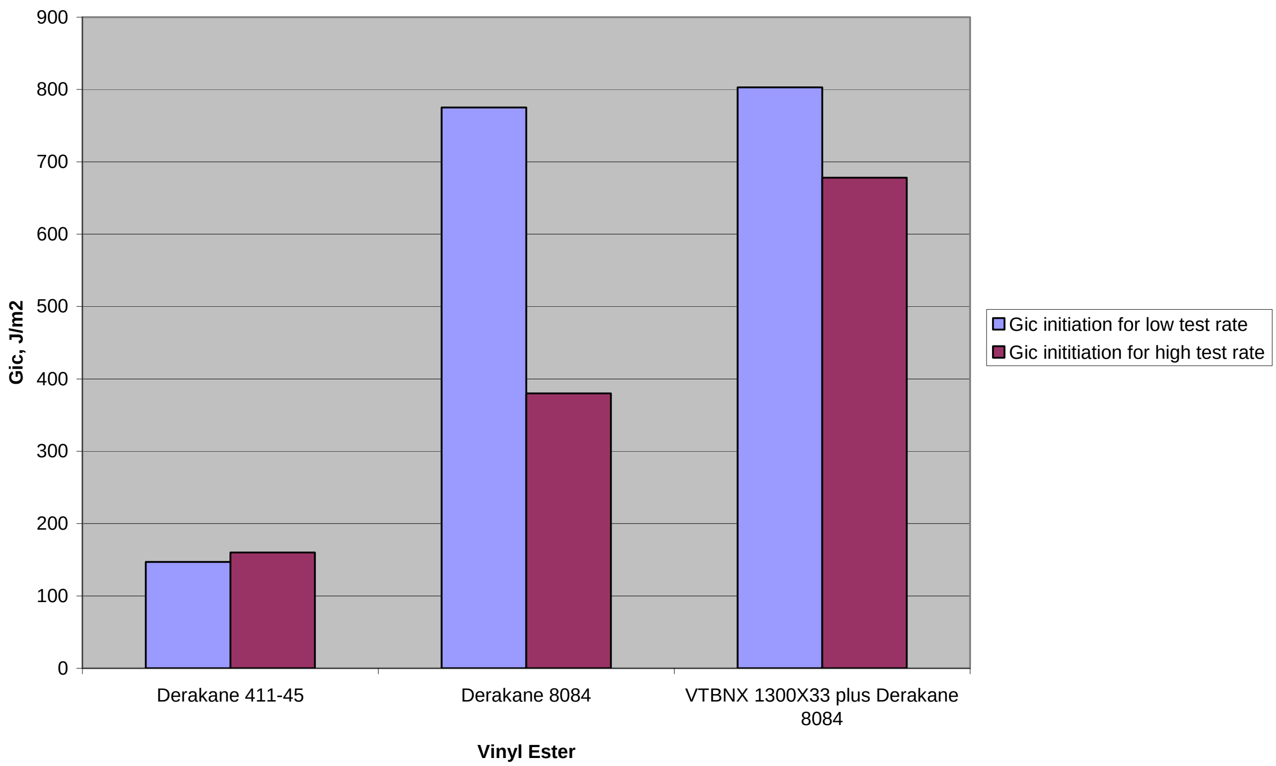
The E-glass used in the Derakane 510A work was 24 oz./yd^2. Recognizably the construction of glass has an effect on delamination resistance of a composite yet the Mode I interlaminar fracture toughness data suggest that a matrix of ETBN 1300X40 modified Derakane 8084 provides an appreciably more crack resistant composite than one based on either Derakane 8084 alone or Derakane 510A.

Derakane 8084 was compared to Derakane 411-45 in unidirectional E-glass continuous rovings (8.9 oz./yd^2) and reported in The Transfer of Matrix Toughness to Composite Mode I Interlaminar Fracture Toughness in Glass-Fibre/Vinyl Ester Composites[1]. In addition a rubber modified Derakane 8084 system was investigated in the form of VTBNX 1300X33. That approach to further toughening vinyl ester resins has been described in Emerald Specialty Polymers literature-AB-259 brochure. The addition of rubber as ETBN 1300X40 or VTBNX 1300X33 to an existing elastomer modified vinyl ester as Derakane 8084 provides sub-micron sized rubber particles for further energy absorption capability.

Double cantilever beam specimen geometry was used for measuring G_{Ic} at two different crosshead displacement rates referred to in the following figures as low rate (2 mm./minute) and high rate (10 mm./minute). This is particularly important as it was noted that Derakane 8084 for an unexplainable reason is rate sensitive.

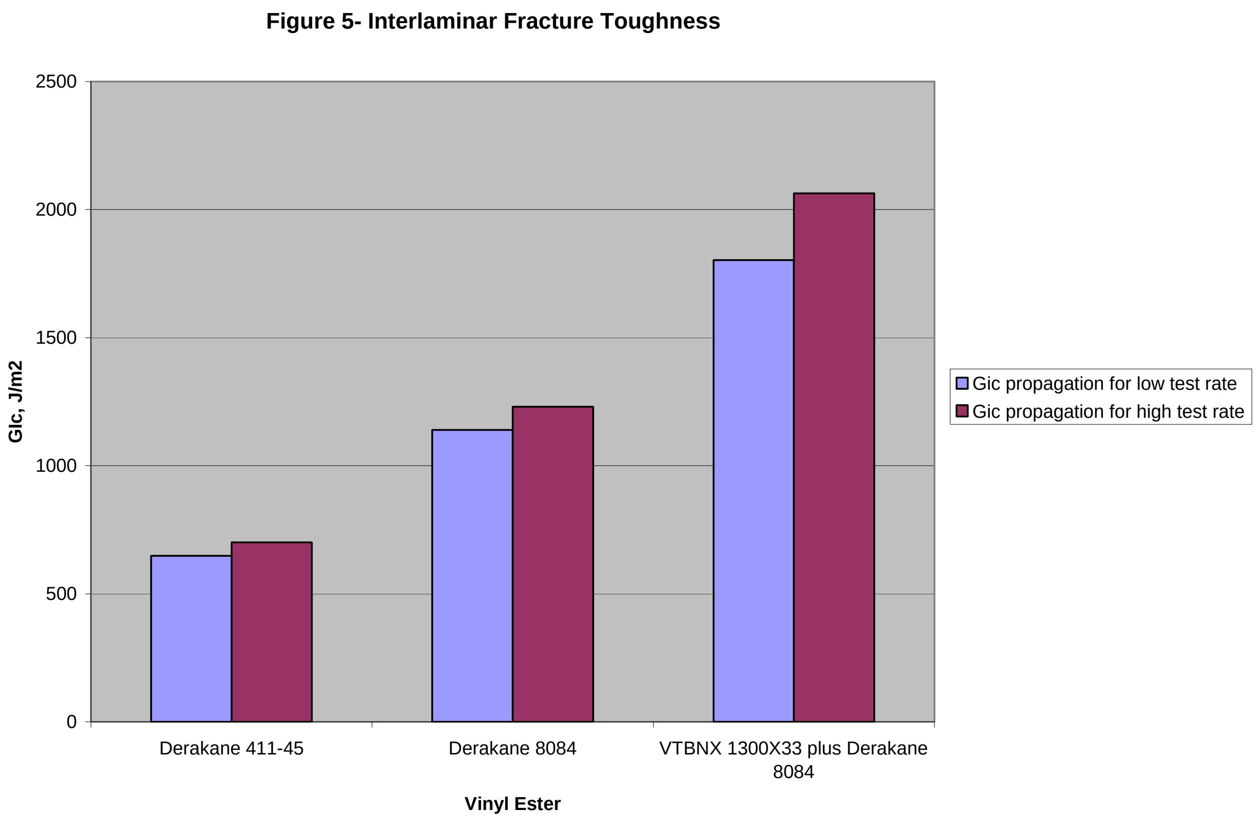
Figure 4 contains crack initiation values for G_{Ic} at low and high testing rates for Derakane's 411-45, 8084 and VTBNX 1300X33 modified Derakane 8084.

Figure 4- Interlaminar Fracture Toughness



Crack initiation values for Derakane 8084 and VTBNX plus Derakane 8084 are less than those cited in Figure 1 realizing that the fiber reinforcement different in the two studies and ETBN 1300X40 was used in the work generating Figure 1 whereas another reactive liquid polymer in the form of VTBNX 1300X33 was used in Derakane 8084 in Figure 4.

Secondly crack propagation for the three resin systems was determined with the absolute value in each case being greater than its respective crack initiation value. That is due to the additional contribution of toughness provided by the fiber bridging. Figure 5 provides such data.



Discussion:

This document serves as one of many that may be found in the literature illustrating enhanced toughness achieved with elastomer modified vinyl ester resins. The practice of modifying a vinyl ester with a reactive liquid polymer has been adopted by resin manufacturers with the advent of Derakane 8084 and similar resins. Such resins may be further toughened by adding ETBN 1300X40 or VTBNX 1300X33. The unique morphology achieved by combining an elastomer with a vinyl ester already containing an elastomer is responsible for the sizable increase in G_{Ic}.

Future Work:

Other elastomer modified vinyl ester resins such as Vipel K018 will be characterized in terms of interlaminar fracture toughness including formulations containing ETBN 1300X40. Double cantilever beams will be exposed to a hot/wet environment to determine how effective the rubber maintains its integrity in composites based on brominated and bisphenol A vinyl esters, e.g. Vipel K018 in the former case and Derakane 8084 in the latter case. Fatigue testing in some capacity will also be considered.

[1] 'Applied Composite Materials' 9: 291-314, 2002

Derakane is Trade Name for Ashland Chemical vinyl ester resins.

Vipel is Trade Name for AOC vinyl ester resins.