ALTERNATIVES IN TOUGHENING
William Starner, Ph.D.

Presented by:
William Starner, Ph.D.
Technical Director
CVC Thermoset Specialties, Inc.
An Emerald Performance Materials Company
**844 North Lenola Road**
Moorestown, NJ 08057
(856) 533-3021
Bill.Starner@emeraldmaterials.com

INTRODUCTION

For over fifty years epoxies have been one of the leaders in the adhesive and structural composite market place. They are typically one or two part systems that offer desirable adhesive and/or crack resistant properties that are maximized in performance by the addition of modifiers. Most conventional modifiers are higher viscosity liquid or solid polymers that cause further thickening to the uncured epoxy formulation making handling more of a challenge. These high formulation viscosities also limit the amount of low cost fillers that can be used. It would be desirable to have a lower viscosity liquid modifier that would not detract from performance but allow for easier handling or the addition of low cost fillers. The modifiers may be compatible in the pre-reaction mix and either remain compatible or phase separate upon curing, [2-5] or may be incompatible in the pre-reaction mix and stay incompatible upon curing.[6-11] An example of a modifier that is compatible in the pre-reaction mix but becomes incompatible (phase separates) during cure would be a carboxy-terminated butadiene acrylonitrile copolymer (CTBN) that may or may not be adducted with epoxy resin.[12-15] CTBNs and adducts with bisphenol A epoxy resin are well known to the industry and should always be used as a benchmark for any epoxy modifier study. These materials are fully miscible with the uncured epoxy resin but phase separate to form spherical inclusions while the epoxy matrix cures. The cure kinetics controls the size and shape of these inclusions. The photos below are SEM micrographs of unmodified (left) and modified (right) cured epoxy formulations. The modifier used on the left was a bisphenol A epoxy resin adducted CTBN (Hypox 1340 based on Hypo 1300X13). The unmodified formulation shows a continuous phase across the photo and the modified formulation shows numerous inclusions where in fact the rubbery phase resides.
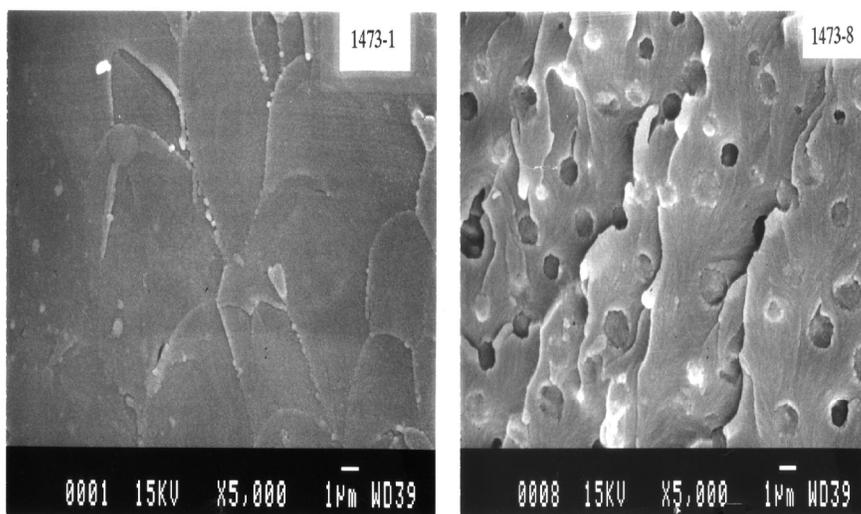
An example of a modifier that is compatible in the premix and also in the cured formula could be a reactive diluent of low molecular weight such as a polyglycidyl ether or ester. These materials do not phase separate at any time before or after the epoxy

matrix cures resulting in a transparent more ductile or elastomeric epoxy. They may be used to enhance adhesion but typically not for structural support. And an example of a modifier that is not compatible at any time before or after cure would be core shell particle or filled or hollow glass bead. Incompatible modifiers do not significantly impact Tg, do not enhance adhesion but do provide toughening. Also, in some instances, the modifier is placed on the curative side of a two-part epoxy formulation as in the case with amine terminated butadiene acrylonitrile copolymers (ATBN). This is typically done to better balance the amounts of each of the two components. Often a multiple of modifiers are used to obtain even more specific performance properties. In obtaining the specific properties desired, more often than not, they are obtained at the expense of other properties. With the exception of incompatible modifiers, modifier addition usually results in the loss of Tg. Any other property associated with epoxies may also suffer such as modulus, adhesion, corrosion resistance or brittleness.

STUDY DESCRIPTION

The present paper's focus is on examining the structure/property relationship of compatible liquid modifiers. The study attempts to show how variation in modifier molecular weight, backbone composition and end group functionality affect the modifier and formulation viscosity or handling properties and the Tg, adhesive and toughness properties of the cured epoxy. Four polymer backbones and 3 end group functions were used in the study. The four polymer backbones were polyether, polyester, polybutadiene and butadiene/acrylonitrile copolymer. The end group functions varied with backbone structure.

For the polyether backbone the end group functionality was restricted to glycidated polyether glycols. Attempts were made using the glycol ethers themselves but as they do not react into the formulation during cure they left the specimens oily and difficult to handle. To investigate the affect of molecular weight and molecular size the glycidyl ethers were synthesized from polypropylene glycols and triols ranging in molecular weight from 425 to 4000. The glycidyl ethers were prepared from the reaction of the representative glycol with epichlorohydrin in the presence of a Lewis acid catalyst followed by dehydrochlorination.[16, 17]

In the case of the polyesters, polybutadiene, and butadiene/acrylonitrile copolymers, all were carboxylic acid terminated and reacted with Bisphenol A epoxy resin to form adduct esters, diglycidyl alkyl ether adduct esters and the glycidyl esters of the carboxylic acids. The polyesters used in this study were Priplast 2101 and 2104. They are dimer acid based polyesters having molecular weights of 1500 and 3000, respectively. The three carboxy terminated butadiene/acrylonitrile copolymers (CTBN) were Hypro 1300X31, 1300X8 and 1300X13. The three CTBNs had molecular weights of 3800, 3550 and 3150, and acrylonitrile contents of 10, 18 and 26%, respectively. The carboxy-terminated polybutadiene (CBT) was Hypro 2000X162 and had a molecular weight of 4200. The Bisphenol A and diglycidyl alkyl ether adducts were prepared by the reaction of the respective epoxide with the carboxy-terminated materials mentioned above.[21, 22] The epoxy terminated adducts are made using an excess of epoxide such that the resulting

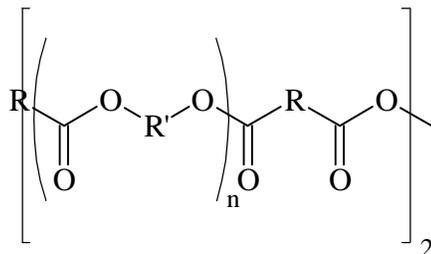product contained 40% and 50%, respectively, of the modifier. The glycidyl esters were synthesized by reacting the carboxy-terminated material with epichlorohydrin followed by dehydrochlorination.[18-20]
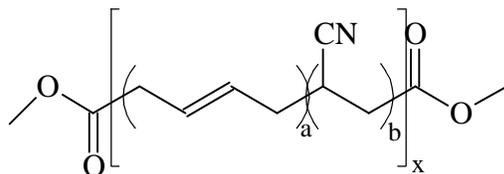
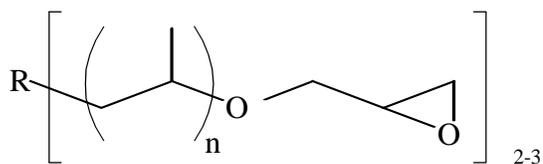## BACKBONE STRUCTURES

Polyether
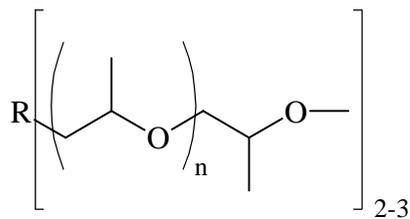
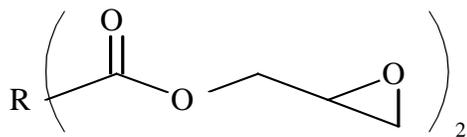Polyester

Butadiene/acrylonitrile copolymer

END GROUP STRUCTURES

Epichlorohydrin Reaction products

Glycidyl Polyethers

Glycidyl CTBNs & Polyesters

MODEL FORMULA AND TEST PROTOCOL

The model formulation for the study employed liquid Bisphenol A epoxy resin, dicyandiamide as curative and Omicure U52M as accelerator. Fumed silica was also added to aid in maintaining the suspension prior to cure. The formulation composition was:

    Bisphenol A liquid epoxy resin
    15% Modifier based on epoxy resin
    6 phr dicyandiamide
    3 phr Omicure U52M
    2 phr fumed silica

For adhesive testing 250-micron glass beads were added to maintain constant adhesive thickness in the bond line. All formulation cures were conducted by heating the specimen to 125°C and holding for 2 hours.

The tests employed and the methods used in this study were:

    Modifier viscosity at 25°C   ASTM D2393
    Mixed formulation viscosity at 25°C   ASTM D2393
    Tg of cured formulation   ASTM E1356
    Lap shear of cured formulation   ASTM D1002
    T Peel of cured formulation   ASTM D1876
    Fracture toughness (K1c) of cured formulation   ASTM D5045

Formulation preparation was to mix all ingredients together at room temperature using a cowls mixer. Applying the mixture to the substrate or pouring the mixture into appropriate mold. This procedure is standard and well known in the industry. Phosphate treated cold rolled steel (1" X 4") was used as the substrate for all lap shear and T peel testing. Phosphate treated cold rolled steel was chosen as the test substrate because this substrate is known for providing the best cohesive bond to epoxy adhesives. The goal is to have predominately adhesive failure so to be sure that the properties of the adhesive are truly being measured.

RESULTS AND DISCUSSION

Glycidyl Polypropylene Glycol Ether Modifiers

Glycidyl polypropylene ether modifiers based upon 425 and 4000 mw polypropylene diol, and 2000, 3000 and 4000 polypropylene triol were prepared by reaction with epichlorohydrin using Lewis acid catalyst followed the dehydrochlorination yielding the corresponding glycidyl ether. There materials were then used as the modifiers in the 'model formulation' and the formulations cured and tested as stated above.

Table 1
**Epoxy formulations using glycidyl polypropylene glycol ethers as modifiers**

Example	1	2	3	4	5	6	7
Modifier	none	425 mw diol	1550 mw triol	2000 mw triol	3000 mw triol	4000 mw triol	4000 mw diol
Modifier Viscosity (cps@ 25°C)	0	75	400	275	420	750	912
Mix Viscosity (cps @ 25°C)	38900	11700	15550	13225	21050	26000	26000
Tg (°C)	134.8	89.72	90.14	106.34	116.78	118.11	120.64
Lap Shear (PSI)	1242	1844	1812	2143	1690	1302	1131
T-Peel (PLI)	7.89	8.3	7.9	13.37	11.85	10.74	8.55
K1c (MN/m$^{1.5}$)	0.56	2.46	2.6	1.91	1.56	1.26	1.29

The modifiers shown here have viscosities ranging from 75 to about 900 cps@25°C. These viscosities are low when compared to the viscosity of Bis A epoxy resin (11,000-14,000 cps @ 25°C) (Table 1). As a result, when used in an epoxy formulation as shown in Examples 2-7 of Table 1, the formulation viscosity is much lower than an unmodified formulation (Example 1, Table 1). These lower viscosities can be quite useful to the formulator as it makes for easier handling and also allows for the use of more fillers.

The Tg of cured formulations varies considerably with molecular weight and molecular size of the modifier. As the molecular weight and size of the modifier increases, the compatibility of that modifier decreases in the cured formulation. Thus, as the modifier increases in molecular weight and size less of an affect on the Tg is observed. Examples 6 and 7 show the influence of molecular size. The modifier in Example 6 is a triol and in Example it is a diol. The diol can be envisioned as larger in a linear fashion, not as compact as a triol, and thus perhaps more incompatible. The data suggests that an even higher molecular weight glycidyl polypropylene glycol ether would give even more incompatibility and thus a Tg closer to the unmodified formulation in Example 1.

The extent of compatibility can be simply observed by looking at the cured specimens (Figure 1). The low molecular weight formulation of Example 2, Table 1, seen in Figure 1a, is completely clear meaning full and complete compatibility within the cured epoxy matrix and thus the low Tg. The 2000 molecular weight modifier of Example 4, Table 1, seen in Figure 1b, shows a slight amount translucency indicating slight incompatibility in the cured formulation and higher Tg. Figure 1c shows an opaque specimen indicating a high level of incompatibility for 4000 molecular weight modifier of Example 7, Table 1.

Figure 1
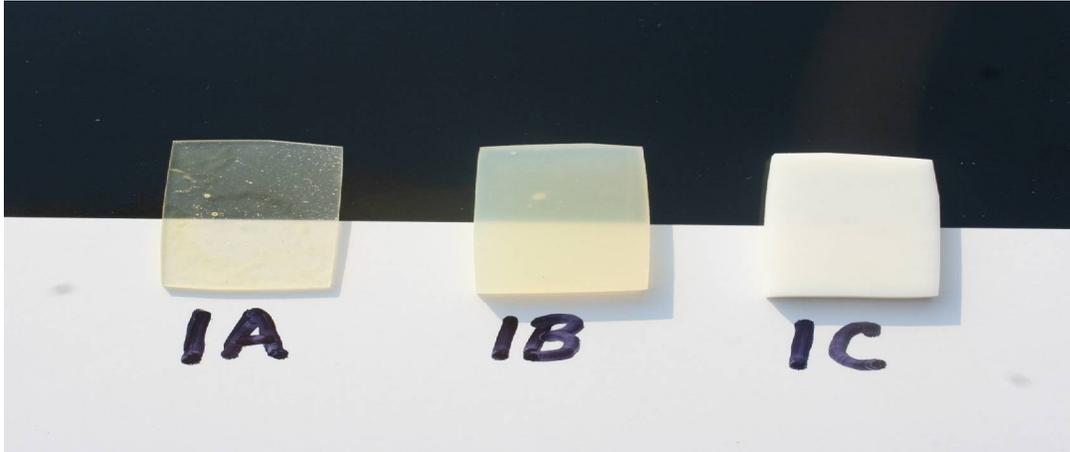
The lap shear and T-peel data shows that adhesion is improved by addition of these modifiers, particularly with those of lower molecular weight. In all likelihood the higher adhesive properties exhibited by the lower molecular weight glycidyl ethers is the result of ductility or flexibility of the cured epoxy formulation imparted by the glycidyl ether solubility in the epoxy matrix.

The fracture toughness measured by K1c is also much higher than that of the unmodified formulation is Example 1. However, the toughness decreases with increasing molecular weight again due to decrease in solubility of the modifier leading to less ductility and more brittleness in the cured epoxy. With the higher molecular weight glycidyl ethers phase separation leads to true fracture toughness due to phase separation of the modifier.

Bisphenol A Epoxy Adducted Modifiers

Four bisphenol A epoxy adducted modifiers were prepared and tested in this study. Two were based on carboxylic acid terminated dimer polyesters, Priplast 2101 and 2104, and the other two were based on CTBNs, Hypro 1300X8 and 1300X13. The polyesters chosen were 1500 and 3000 molecular weight and the CTBNs chosen had acrylonitrile contents of 18 and 26 % and molecular weight of 3550 and 3150. The adducts were synthesized by the reaction of the carboxylic acid terminated polymers (40 parts) with an excess of Bisphenol A epoxy resin (60 parts) using triphenylphosphine as catalyst. The formulations were adjusted such that the modifier content was maintained at 15% for all. For example, when the modifier was in the pure state the formulation contained 15% modifier out of a 100% total of Bisphenol A epoxy resin and modifier. For these adducts the modifier content in the formulation was 35% so that the modifier level was still 15%. All formulations were cured as above.

The viscosities of these modifiers (Table 2) ranging from about 100,000 to 450,000cps @ 25°C are inherently higher than the viscosity of the Bisphenol A epoxy resin used in the formulation because the adduction process. The adduction process generates

oligomers with the resin generating higher molecular weight species. As a result of these high modifier viscosities the formulation viscosities, observed for Examples 8-11, are also quite high compared to the unmodified Example 1. As Bisphenol A epoxy resin adducts are the most widely used modifiers in the industry this high viscosity has to be accommodated by the use of more specialized and costly formulating process equipment and also limiting the amount of low cost filler that can be used. Lower viscosity modifiers are always being requested by the industry.

   Here again in this study, the Tg of the cured modified formulations are about 15 to 25°C lower than the unmodified formulation. This again is due to some level of compatibility of the modifier in the epoxy matrix. Although the molecular weight of these adducts are higher there is a compatibility factor that comes into play because of the Bisphenol A epoxy moiety now a part of the molecule enhancing compatibility. In comparing the Tgs of Examples 8, 9, 10 and 11, it shows that the Tg increases with molecular weight and does not appear to be associated with the polymer backbone composition.

    With the exception of Example 8, which shows lower lap shear, overall the lap shear and T'peel adhesive properties are far better than the standard and quite similar to each other. Example 11 exhibits a bit higher adhesive strength probably because of higher polarity from the increased acrylonitrile content. As both polymer backbones are known to exhibit good adhesive properties these findings are not unexpected.

Table 2
Epoxy formulations using bisphenol A epoxy adducted esters as modifiers

Example	1	8	9	10	11
Modifier	none	1500 mw	3000 mw	3550 mw	3150 mw
		Polyester	Polyester	18% AN	26% AN
		Adduct	Adduct	CTBN adduct	CTBN adduct
Modifier Viscosity (cps@ 25°C)	0	131500	106750	200000	450000
Mix Viscosity (cps @ 25°C)	38900	106000	96000	117500	157000
Tg (°C)	134.8	106.11	113.01	117.7	112.6
Lap Shear (psi)	1242	1507	2317	2211	2421
T-Peel (pli)	7.9	15.65	17.5	17.3	19.01
K1c (MN/m$^{1.5}$)	0.56	2.04	1.93	1.33	1.65

Fracture toughness properties within the set are quite good compared to the unmodified formulation. The polyesters of Examples 8 and 9 are better than the CTBN adducts of Examples 10 and 11. Looking at the Tgs of the two sets would indicate that the improved K1c in Examples 8 and 9 are because of more ductility in the epoxy matrix because of more compatibility. Again there is a relationship showing that molecular weight has an affect on Tg, compatibility and toughness.

Glycidyl Ester Modifiers

Glycidyl ester modifiers based on 3000 molecular weight carboxylic acid terminated polyester (Priplast 2104), a 4200 molecular weight carboxylic acid terminated polybutadiene (Hypro 2000X162) and three butadiene/acrylonitrile copolymers (Hypro 1300X31, 1300X8 and 1300X13) having molecular weight of 3800, 3550 and 3150 and containing 10, 18 and 26 % acrylonitrile respectively. These materials were synthesized by the reaction of the carboxylic acid group with epichlorohydrin followed by dehydrochlorination with base generating the glycidyl ester. These materials, shown in Table 3, Examples 12, 13, 14, 15 and 16, have viscosities ranging from about 40,000 to about 576,000 cps @ 25°C. These viscosities are lower than viscosities seen for the bisphenol A epoxy adducted materials in Table 2, keeping in mind that the industry benchmark is Example 11. This is due to the fact that they are not oligomeric but simple esters. Also the mix viscosities of the formulated products made from these glycidyl esters have a significantly lower viscosity than their adduct counterparts for two reasons. One, as just stated, they are simple glycidyl esters and not oligomeric and secondly because the entire molecule is the modifier it is used at a 15% loading rather than the 35% used for bisphenol A epoxy adducts in Table 2.

Table 3
Epoxy formulations using glycidyl esters as modifiers

Example	1	12	13	14	15	16
Modifier	none	3000 mw	4200 mw	3800 mw	3550 mw	3150 mw
		Glycidyl	Glycidyl	Glycidyl	Glycidyl	Glycidyl
		Polyester	CTB	CTBN	CTBN	CTBN
			0% AN	10% AN	18% AN	26% AN
Modifier Viscosity (cps@ 25°C)	0	38500	43900	79200	120900	576000
Mix Viscosity (cps @ 25°C)	38900	47800	40200	50000	60600	68900
Tg (°C)	134.8	116.91	126.2	122.3	124	123.6
Lap Shear (psi)	1242	1914	2100	2381	2477	2468
T-Peel (pli)	7.89	17.6	13.4	28.4	20.9	21.3
K1c (MN/m$^{1.5}$)	0.56	1.8	1.38	1.35	1.31	1.43

Comparing the Tgs within the set in Table 3 with the unmodified formulation, Example 1, it is seen that they are again lower indicating that there is some portion of the modifier still compatible with the epoxy matrix. However, a comparison of these Tgs with that of the two previous studies (Tables 1 & 2) shows that these glycidyl esters are less compatible and have less of an affect on the Tg. Within the set of Examples 12, 13, 14, 15 and 16 the Tg follows along again with the concept that higher molecular weight gives higher Tg and less compatibility in the epoxy matrix.

The adhesive properties as expressed by lap shear and T'peel are much improved over the unmodified formulation in Example 1. The adhesive properties of the glycidyl butadiene/acrylonitrile copolymers appear to be better than either the glycidyl polyester or the glycidyl polybutadiene. A comparison of the glycidyl esters (Table 3) with the bisphenol A adducts (Table 2) with the similar backbone is indicates that the glycidyl esters provide better adhesive properties and higher Tgs at lower formulation viscosities.

Addition of the glycidyl ester modifiers shows good improvement in fracture toughness compare to the unmodified formulation. It would appear that the 3000 molecular weight glycidyl ester shown in Example 12, Table 3 exhibits the highest K1C value yet the lowest Tg. This is again may be indicative of ductility from some compatibility with the epoxy matrix. The glycidyl polybutadiene ester and all the glycidyl butadiene/acrylonitrile copolymer esters, Examples 13, 14, 15 and 16, generate similar K1c values.

Alkyl Epoxy Adducted Ester Modifiers

These modifiers are adducts prepared by the reaction of a diglycidyl alkyl ether with a carboxylic acid terminated butadiene/acrylonitrile. The alkyl moieties used in this study were based on neopentyl glycol and cyclohexanedimethanol. These diglycidyl glycidyl ethers are well known to the industry as diluents. These adduct types are prepared in the same fashion as the bisphenol A epoxy adducts described above. An excess of the diglycidyl ether is again used to minimize high oligomer formation. In the case of these adducts the ratio of diglycidyl ether to the carboxy-terminated butadiene/acrylonitrile copolymer is 50/50. As a result, the formulation contains approximately 15% diglycidyl ether diluent, which is known to affect the cured formulation properties. The formulation for this study was 30 parts alkyl epoxy adduct ester and 85 parts bisphenol A epoxy resin. All other materials remained the same as in the other previous studies. In the case of the neopentyl diglycidyl ether adduct the polymer backbone was the carboxy-terminated butadiene/acrylonitrile copolymer (Hypro 1300X13) with a molecular weight of 3150 and an acrylonitrile content of 26% and the cyclohexanedimethanol diglycidyl ether adduct backbone was carboxy-terminated butadiene/acrylonitrile copolymer (Hypro 1300X8) with a molecular weight of 3550 and a acrylonitrile of 18%.

Table 4
Epoxy formulations using alkyl epoxy adducted esters as modifiers

Example	1	17	18
Modifier	none	3150 mw	3550 mw
		CTBN	CTBN
		26% AN	18% AN
		Neopentyl glycol	Cyclohexane
		diglycidyl ether	dimethanol
		Adduct with	diglycidyl ether
			adduct
Modifier Viscosity (cps@ 25°C)	0	6000	20000
Mix Viscosity (cps @ 25°C)	38900	31400	50400
Tg (°C)	134.8	102.4	106.6
Lap Shear (psi)	1242	2314.1	1958
T-Peel (pli)	7.89	12.00	9.50
K1c (MN/m$^{1.5}$)	0.56	0.79	1.17

The viscosity of these adduct esters (Examples 17 & 18) are low resulting in formulation mix viscosity. The lower viscosity is the result of the 50% excess diglycidyl ether used in the adduct synthesis. By comparison, the bisphenol A ester adducts shown in Table 2 range from about 100,000 to 500,000 cps @ 25°C and the alkyl epoxy ester adducts in Table 4 range in viscosity from 6,000 to 20,000 cps @ °C, a factor of at least 20.

Although these modifiers provide low viscosity there affect on Tg is quite negative. A comparison of Example 17 and 18 with the unmodified in Example 1 shows a 30 to 32°C loss in Tg.

The adhesive properties of Examples 17 and 18 compared to that of the unmodified in Example 1 show good improvement and the K1c toughening properties are better.

Study Comparison

To see how each of the best in each study above compares with one another, the best performing formulas from the set of Glycidyl Polypropylene Glycol Ether Modifiers, Bisphenol A Epoxy Adducted Ester Modifiers and Glycidyl Ester Modifiers were selected and compared in Table 5. The best of the Alkyl Epoxy Adducted Ester Modifiers study was not selected for this discussion as the performance of these materials were far lower than the other three studies and the lessons learned in this study can be discussed and understood in their absence. The formulas chosen are Examples 3, 7, 9, 11, 12, 13 and 16. Examples 3 and 7 represent the best from the Glycidyl Polypropylene Glycol Ether Modifiers study in Table 1. Examples 9 and 11 represent the best from Bisphenol A Epoxy Adducted Ester Modifiers study in Table 2. And Examples 12, 13 and 16 represent the best from the Glycidyl Ester Modifiers study in Table 3. A mentioned earlier, Example 11 is well known standard modifier in the adhesive and composite industry and may be used as a benchmark in this study. Looking through this series a number of observations can be made.

The Glycidyl Polypropylene Glycol Ether Modifiers (Examples 3 and 7)

- Have the lowest modifier and mix viscosity within the series.
- The 1550 molecular weight glycidyl polyether is the lowest molecular weight in the series and thus the highest compatibility and lowest Tg.
- The 4000 molecular weight glycidyl polyether is the second highest molecular weight and the third highest in Tg.
- The T'peel strength of the glycidyl polyether are poor compared to the others within the series.
- The lap shear strength follows molecular weight and compatibility.
- The 1550 molecular weight glycidyl ether has the highest K1c value for fracture toughness within the series, which is believed to be due to ductility and elasticity imparted by the compatible modifier.

Bisphenol A Epoxy Adducted Ester Modifiers (Examples 9 and 11)

- The modifier and mix viscosities are the highest within the series and would be expected because of the high molecular weight of the adduct.
- Regardless of backbone similar Tgs are observed as the molecular weight is similar and the end group adduct provides similar compatibility in the cured epoxy matrix.
- The adhesive properties are near the highest within the series as the polyester backbone is known to provide good adhesion.
- The fracture toughness is quite good again due to the backbone structure.
- Example 11 is a benchmark for performance.

Table 5
Performance comparison of the best of the study

Example	3	7	9	11	12	13	16
Modifier	1550 mw	4000 mw	3000 mw	3150 mw	3000 mw	4200 mw	3150 mw
	Glycidyl	Glycidyl	Polyester	26% AN	Glycidyl	Glycidyl	Glycidyl
	Ether triol	Ether diol	Adduct	CTBN adduct	Polyester	CTB	CTBN
						0% AN	26% AN
Modifier Viscosity (cps@ 25°C)	400	912	106750	450000	38500	43900	576000
Mix Viscosity (cps @ 25°C)	15550	26000	96000	157000	47800	40200	68900
Tg (°C)	90.14	120.64	113.01	112.6	116.9	126.2	123.6
Lap Shear (psi)	1812	1131	2317	2421	1914	2100	2468
T-Peel (pli)	7.9	8.55	17.5	19.01	17.6	13.4	21.3
K1c (MN/m$^{1.5}$)	2.6	1.29	1.93	1.65	1.80	1.38	1.43

Glycidyl Ester Modifiers (Examples 12, 13 and 16)

- The modifiers and, more so, the mix viscosities of these modifiers are far lower than the epoxy adduct modifiers of Examples 9 and 11 but not as low as the glycidyl ethers of Examples 3 and 7. As Example 11 would be considered a benchmark, the lower mix viscosities of the glycidyl esters would be an advantage for the industry.
- The Tgs are the highest in the study due to high molecular weight and low compatibility effects by the glycidyl terminus.
- The adhesive and toughening properties are equal to slightly better than the industry benchmark, Example 11.

SUMMARY AND CONCLUSION

The present paper clearly shows that glycidyl ether and ester modifiers provide significant advantages compared to the unmodified formulation and the CTBN based industry benchmark.

- The glycidyl ether and ester modifiers are lower in viscosity and yield lower formulation mix viscosities than the industry benchmark.
- Selection of the proper glycidyl ether or ester will allow for higher Tg and desired adhesive and toughener performance.

- The Tg of the cured epoxy formulation is dependant on the molecular weight of modifier and the terminal group functionality but not so much on the backbone structure.
- A Tg comparable to an industry standard, such as bisphenol A epoxy adduct of butadiene/acrylonitrile copolymer with 26% acrylonitrile and molecular weight 3150, Example 11 can be reached only if the polymer backbone has a molecular weight of greater than 2000.
- The end group functionality appears to affect compatibility is the cured epoxy matrix thus Tg is affected. Glycidyl ethers and esters exhibit less compatibility than epoxy adducts and thus give higher Tg at the same molecular weight.
- The study shows that adhesive properties are affected by the polymer backbone. Both polyester backbones and butadiene/acrylonitrile copolymer backbones provide better adhesion compared to glycidyl polyethers.

REFERENCES

1. Ashcroft, W. R., *Chemistry and Technology of Epoxy Resins,* Ellis, B. Ed.; Blackie Academic & Professional; London, 1993, 37-71.
   Lee, H. and Neville, K., *Handbook of Epoxy Resins,* McGraw-Hill Book Company, New York.
   May, C. A., *Epoxy Resins Chemistry and Technology, Second Edition, Revised and Expanded,* Marcel Dekker, Inc.; New York, 1988.
2. Sultan, J. N. and McGarry, F., *J. Polym. Eng. & Sci.* 1973, *13*, 29-34.
3. Pearson, R. A. and Yee, A. F., *J. Mat. Sci.* 1986, *21,* 2462-2474.
4. Pearson, R. A. and Yee, A. F., J. Mat. Sci. 1986, 21, 2475-2488.
5. Pearson, R. A. and Yee, A. F., J. Mat. Sci. 1989, 24, 2571-2580.
6. Sue, H. J.; Bertram, J. L.; Garcia-Meitin, E. I.; Wilchester, J.W.; Walker, L.L. Coll. Polym. Sci. 1994,272,456-466.
7. Lin, K. F. and Shieh, Y. D., J. Appl. Polymer International, 1998, 70, 2313-2322.
8. Day, R. J.; Lovell, P. A.; Pierre, D. Polymer International, 1997, 44, 288-299.
9. Lee, J. and Yee, A. F. Polymer 2000, 41,8375-8385.
10. Lee, J. and Yee, A. F. Polymer 2000, 41,8363-8373.
11. Lee, J. and Yee, A. F. Polymer 2001, 42,577-588.
12. Cech, J. and Kretow, R. The Effectiveness of Toughening Technologies on Multifunctional Epoxy Resin Systems, SPI Conference 2001.
13. McGarry, F. J. and Willner, A. M. *Toughening of an Epoxy Resins by an elastomeric Second Phase,* Res. Rept. R68-8, School of Engineering, Massachusetts Institute of Technology, Cambridge, Mass.1968.
14. Sultan, J. N. and McGarry, F. J. *Macrostructural Characteristics of Toughened Thermoset Polymers, Ibid*, R69-59, 1969.
15. Rowe, E. H.; Siebert, A. R.; Drake, R. S. *Mod. Plast.* 1970 *417,* 110.
16. Hueter, R.; Waldfrieden, H.; Anhalt, R. *Washing-out, Washing, Cleansing, Lathering, and Dispersing Agents,* U. S. Patent 2,094,489 to Unichem, 1937.

17. Whyte, D. D. and Korpi, E. O. *Alkyl Gylceryl Ether Sulfonate Mixtures and Processes for Preparing the Same,* U. S. Patent 3,024,273 to The Procter and Gamble Company, 1962.
18. Baumann, D. and Habermeier, J. *Long-chain Diglycidyl Esters*, U. S. Patent 3,784,525 to Ciba-Geigy Corp. 1974.
19. Heer, A. and Schaffner, W. *Diglycidyl Esters of Aliphatic Dicarboxylic Acids,* U. S. Patent 3,644,431 to Ciba Limited, 1972.
20. Gruver, J. T. and Kraus, G. *Polymer Compositions Using Liquid Carboxy-terminated Diene Polymer and Epoxidized Compound,* U. S. Patent 3,208,980 to Phillips Petroleum Co., 1965.
21. Mueller, A. C. *Process for Preparing Epoxy Esters,* U. S. Patent 2,772,296 to Shell Development Co. 1956.
22. Unknown *Process for the Preparation of Epoxide Resins,* Britain Patent 884.033.