CVC Thermoset Specialties	Technical Service Report	TSR081029-CZ Author: Charles Zarnitz

Flexibilizing Modifiers

Objective

The primary objective of this report is to discuss the various types of Flexibilizing Modifiers available from CVC. Secondarily, we will discuss curing agent selection, the differences between flexibilization and toughening, and will show data and trends one can expect to see with our various flexibilizing modifiers.

CVC currently manufactures 6 products that can be described as flexibilizing modifiers. In addition we make a Flexibilizing Resin, HyPox DA323 which will not be covered in detail for this report. The Flexibilizing Modifiers are as follows;

- Erisys GE-23 – Diglycidyl Ether based on Dipropylene Glycol
- Erisys GE-24 – Diglycidyl Ether based on Polypropylene Glycol
- Erisys GE35 and GE35H – Triglycidyl Ethers based on Castor Oil
- Erisys GE-36 – Triglycidyl Ether based on Propoxylated Glycerin
- Erisys GS-120 – Diglycidyl Ester based on Dimer Acid

<u>1. Erisys GE-23</u> – GE-23 is the Diglycidyl Ether of Dipropylene Glycol. It has a structure as shown below.

n= 2

GE-23 has a viscosity range of 30 to 60 cps at 25°C and EEW range of 175 to 205 grams/equivalent.
A special low viscosity grade of this product is available and is designated GE-23LV. It has a viscosity range is 20 to 34 cps and EEW range 160 to 180 grams/equivalent.

<u>2. Erisys GE-24</u> – GE-24 is the Digylcidyl Ether of Polypropylene Glycol. It has a structure as shown below.

n = 7

GE-24 has a viscosity range of 55 to 100 cps at 25°C and EEW range of 305 to 335 grams/equivalent.

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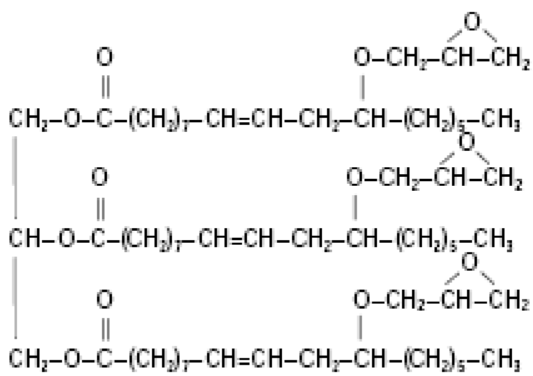
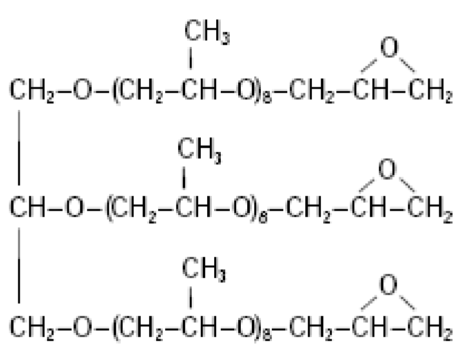
3. Erisys GE-35 and 35H – GE-35 and GE-35H are each designated as the Triglycidyl Ether of Castor Oil. Specific differences in processing during the manufacture of these products results in subtle but important differences in finished product application properties. Each product is made to the same specification with respect to viscosity and EEW. GE-35 and 35H have a structure as shown below.



GE-35 and 35H have viscosity ranges of 300 to 500 cps at 25°C and EEW range of 550 to 650 grams/equivalent. GE-35 will yield cured product with higher modulus at higher dilutions while GE-35H will provide for more flexible cured product.
These products are useful to modify the flexibility of standard bisphenol A type epoxy resins. However, they may not be compatible with some Epoxy Phenol Novolac (EPN) Resins and may separate on standing if mixed with EPN resins, particularly higher molecular weight EPN's.

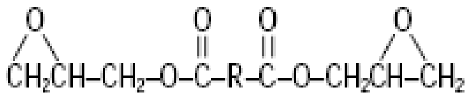
4. Erisys GE-36 – GE-36 is the Triglycidyl Ether of Propoxylated Glycerin. This product has a structure as shown below.



GE-36 has a viscosity range of 200 to 320 cps at 25°C and EEW range of 620 to 680 grams/equivalent.

5. Erisys GS-120 – GS-120 is designated as the Diglycidyl Ester of Dimer Acid. This product has a structure as shown below.

Flexibilizing Modifiers



$R=C_{34}H_{68}$

GS-120 has a viscosity range of 400 to 900 cps at 25°C and EEW range of 390 to 470 grams/equivalent.
GS-120 can be used to modify standard bisphenol A type epoxy resins and HyPox DA323. However, it is not compatible with Epoxy Phenol Novolac (EPN) Resins and will separate on standing if mixed with EPN resins.

HyPox DA323

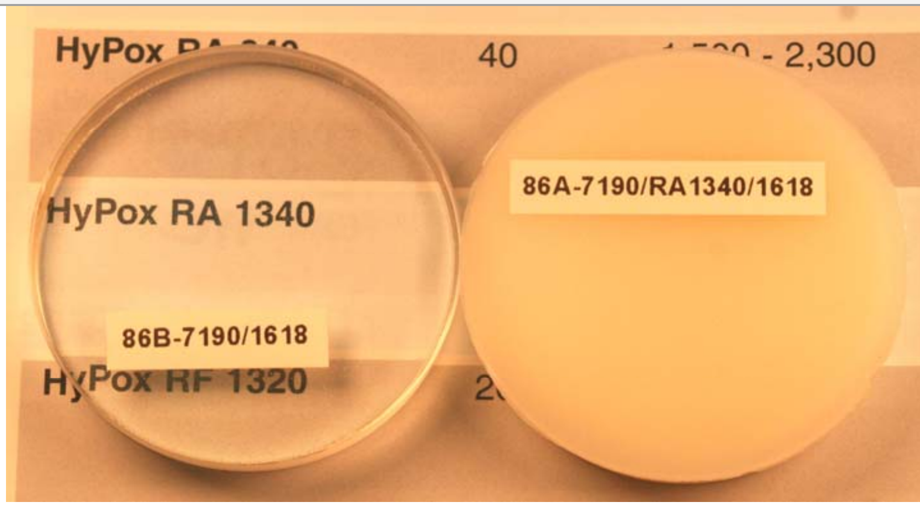
HyPox DA323 is another flexibilizing product from CVC but is more properly classified a resin rather than a modifier. This product provides cured systems that exhibit improved toughness, resilience, durability, and thermal shock. It is a high viscosity semi-solid that requires heat for proper processing. HyPox DA323, like Erisys GS-120, is based on Dimer Acid. The difference is that HyPox DA323 is a reaction product or adduct of the Dimer Acid and standard Bisphenol A Epoxy Resin (LER) while GS-120 is epoxidized Dimer Acid (i.e., the reaction product of Dimer Acid and Epichlorohydrin). HyPox DA323 can be used as a stand alone resin whereby GS-120 should only be used as a flexibilizing modifier. Because of its identical backbone, GS-120 is the ideal modifier to use to reduce the viscosity (and further improve the flexibility) of HyPox DA323.

Flexibilization and “Rubber” Modified Products; Toughened vs. Flexible

A fair amount of confusion exists in our industry with respect to the “flexibilizing” potential of products classified as “Rubber Modified”. Many users make the assumption that, because materials are rubber modified, they must add flexibility and/or elasticity to systems in which they are used. This is not the case. CVC has a large range of products in our HyPox series of products that are labeled as rubber modified. These include the following products;

RA 840
RA 1340
RF 1320
RF 1341
RF 928
RF 933
RM 20
RM 22
RK 84

These rubber modified products do not add flexibility or elasticity to formulated systems. They add toughness via phase separation which occurs during cure to create small micelles of rubber within a primary phase of cured epoxy. The bulk physical properties, such as compressive strength/modulus and glass transition temperature take on the characteristics of the primary phase. The secondary phase acts to arrest crack development increasing the toughness of the system. This rubber toughening effect can be seen in unfilled systems. Toughened systems will turn opaque due to the presence of the secondary (rubber) phase as shown below. The sample on the left has no rubber modifier while the sample on the right has approximately 15 parts of rubber per 100 parts of resin.



Toughened systems have two important characteristics;

1. Greater energy requirement to propagate cracks.
2. Little or no sacrifice in load bearing capabilities, modulus, and Tg.

Flexibilized systems will also exhibit greater energy to propagate cracks but will do so with significant loss in modulus and Tg.

A comparison of the effects on physical performance properties between flexiblizers and tougheners is shown in the table below.

Flexible vs. Toughened Systems -- Comparison vs. Unmodified Formulation

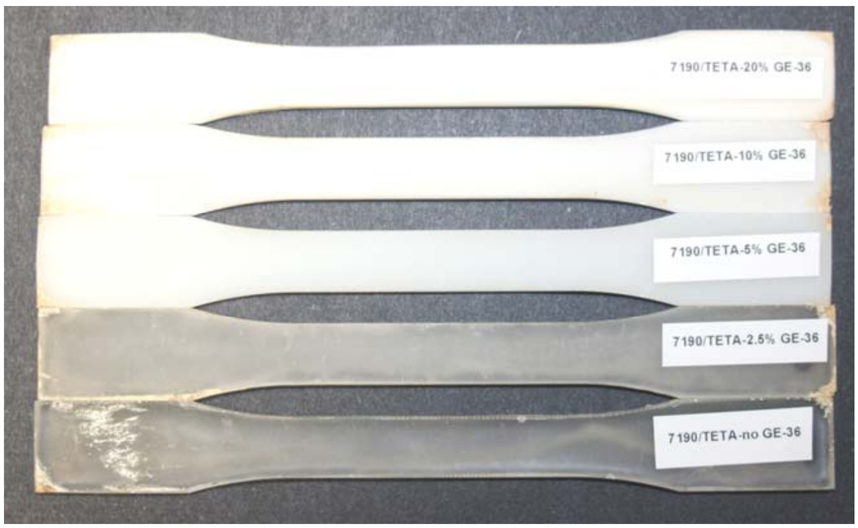
Property	Flexible System	Toughened System
Elasticity	More Elasticity	Unchanged
Brittleness	Much Less Brittle	Much Less Brittle
Tg	Decreased	Unchanged or Slight Decrease
Modulus	Decreased	Unchanged
Peel Adhesion	Improved	Improved
Shear Adhesion	Improved	Improved
Tensile Strength	Decreased	Unchanged
Flexural Strength	Decreased	Unchanged
Compressive Strength	Decreased	Unchanged
Crack Resistance	Improved	Improved

Toughness and Flexibility of Erisys GE-36

Flexibilizing Modifiers

Erisys GE-36 is somewhat unique among flexibilizing modifiers in that it can exhibit the characteristics of a toughener or a flexibilizer depending on the curing agent used. The toughening effect is apparent from the appearance of GE36 modified Epalloy 7190 specimens cured with TETA as shown in the photograph below. In this series the amount of GE-36 increases from zero to 20% (from bottom to top). As we saw previously with the sample of RA1340 modified Epalloy 7190, phase separation (as characterized by the opacity of the cured samples) will occur on cure with this system and the degree of opaqueness increases with the amount of GE-36 in the system.

Epalloy 7190 Modified with GE-36 and Cured with TETA



Furthermore, evidence of toughening can also be seen in the effect on Tg in these formulated systems. In keeping with the characteristics of toughened systems we see the effect on Tg with GE-36 is minimized while a true flexibilizer like GE-24 shows much greater decrease in Tg with increasing concentration.

Tg (°C) vs. % Modifier in Epalloy 7190 -

	0%	5%	10%	20%	30%
GE-24	116	108	93	77	64
GE-36	116	108	106	105	102
Cured with TETA; gel at RT + 2 hours at 100°C					

However, other curing agents will not produce the same effect. In the following photograph we see the same modified resin series mentioned above, but here the curing agent is Jeffamine D-230, a polyoxyalkyleneamine curing agent. In this example there is no phase separation on cure and no toughed character to the cured system. The reason for this difference is likely due to differences in the solubility characteristics of the system.

Epalloy 7190 Modified with GE-36 and Cured with Jeffamine D-230

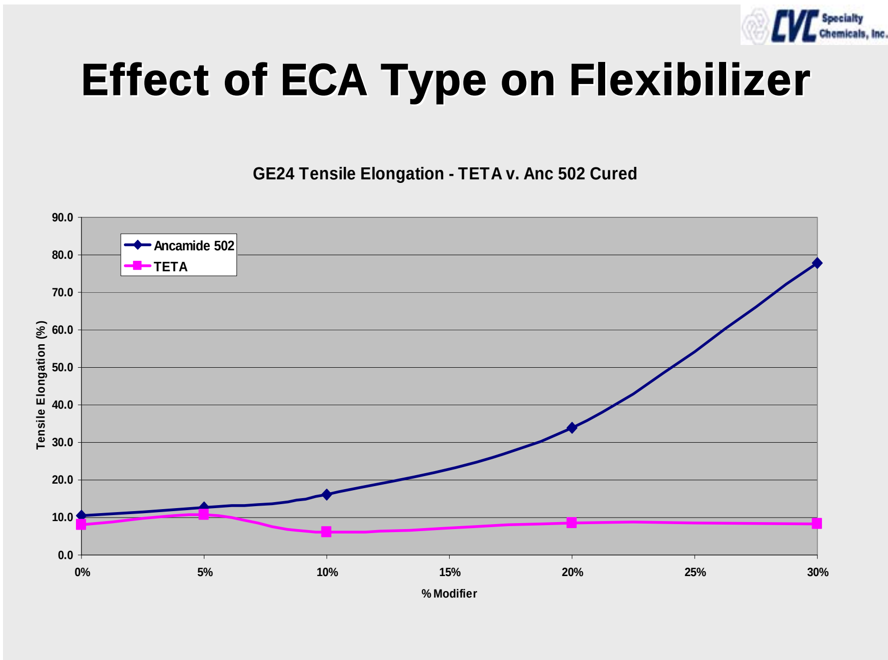
Compatibility of Flexibilizers in Formulated Systems

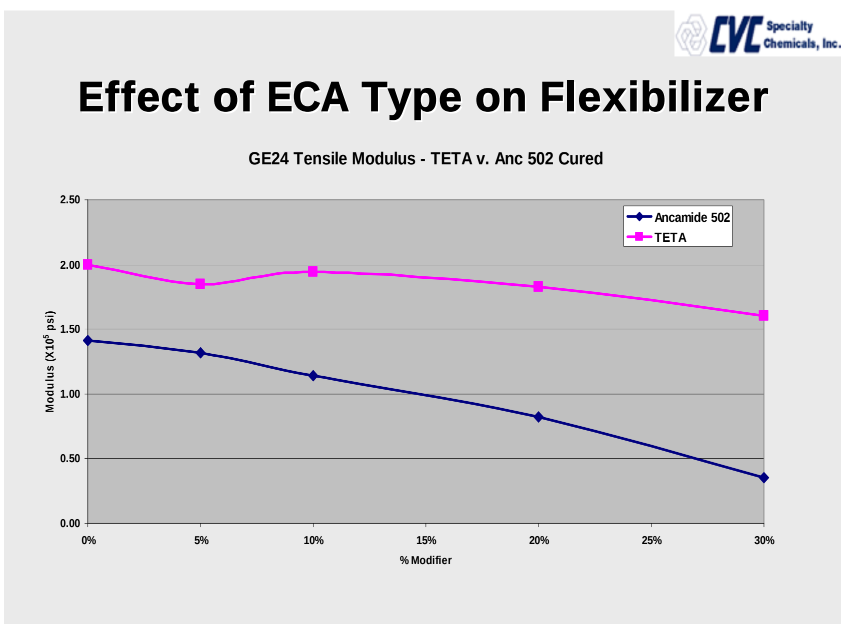
In general, all the flexibilizers mentioned in this report are compatible with LER (Liquid Epoxy Resin). By compatible, we mean mixed systems of flexiblizers and resin do not separate on standing. However, this is not the case with Epoxy Phenol Novolac (EPN) resins, where the solubility characteristics are sufficiently different to show differential compatibility with some flexibilizers. We have found that GE-23, 24, and 36 are generally compatible with the liquid EPN's (8230, 8240, 8250). GE35, GE35H, and GS120 are generally not compatible with liquid EPN's. Keep in mind that this evaluation was done with binary systems only (resin + flexibilizer). Other liquid components of a formulated system may affect the compatibility. To test compatibility, one would mix the liquid components together and then observe over a period of time to see if any separation occurs. Storage at slightly elevated temperatures will accelerate separation if it is to occur.

In addition, one should not confuse the lack of compatibility of the liquid system (generally an undesirable situation) with incompatibilities that develop on curing. As mentioned in the previous section on "Toughness and Flexibility", some systems phase separate on cure due to a component that becomes incompatible on cure. This may be a desirable situation if one wishes to formulate a toughened system. But if the objective is to make a flexible system, phase separation is an undesirable characteristic, as it will detract from flexibilization. To determine if phase separation occurs, one should mix together the liquid components of their system (no fillers, pigments, thixatropes, etc.) with the curing agent, pour out a thin casting, and allow to cure. If the casting remains clear, this indicates no phase separation is occurring and flexibilization is not being compromised by phase separation. If the casting turns opaque or translucent, phase separation is occurring and the flexibility of the system will be less than expected.

Other Effects of Curing Agents on Physical Performance Properties of Flexibilizers

Curing agent chemistry and functionality varies widely. Polyoxyalkyleneamines (Like Jeffamine D230 and D400) and Amidoamines (like Ancamide 502) are designed to provide higher degrees of flexibility than ethyleneamine curing agents like TETA, which will promote higher crosslink density. The relative effect of curing agent selection on Tensile Elongation and Modulus of GE-24 modified systems cured with Ancamide 502 vs. TETA can be seen in the following graphs. As we can see, TETA cured systems show almost no change in elongation, and minimal decrease in modulus as the concentration of GE-24 increases. But when Ancamide 502 is used, the effect of increasing flexibilizer concentration on elongation and modulus is large. This is a result of the functionality of the curing agents. TETA is multifunctional, so even if larger amounts of modifier are used, the effects are minimal because the system is still highly cross linked. When Ancamide 502 is used, the crosslink density is decreased and the elongation and modulus is substantially affected as modifier levels are increased.





Flexibilizing Modifiers

Affect of Flexibilizing Modifier on Perfomance Properties

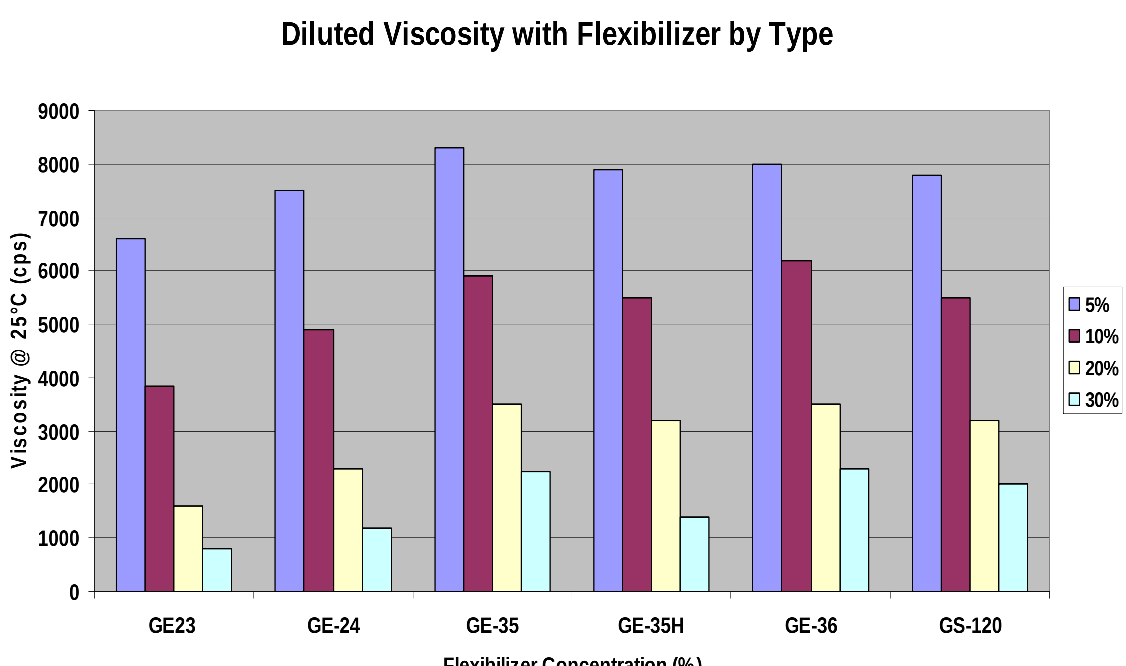
Each flexibilizing modifier will affect performance properties in different ways. The choice of flexibilizer to use for a given application depends on which properties are more important. As with other components of the formulated system, there are trade-offs in the selection of one modifier against another. The following section points out the advantages and disadvantages in the selection of one modifier vs. another for the given range of performance properties considered.

- Viscosity

Each of the flexibilizing modifiers is lower in viscosity than standard LER and will affect a decrease in viscosity over neat LER. The magnitude of the decrease is dependent on the base viscosity of the modifier. Typical viscosity ranges for neat modifiers are as follows;

	GE-23	GE-24	GE-35	GE-35H	GE-36	GS-120
Viscosity Range (cps @ 25°C)	30 - 60	55 - 100	300 - 500	300 - 500	200 - 320	400 - 900

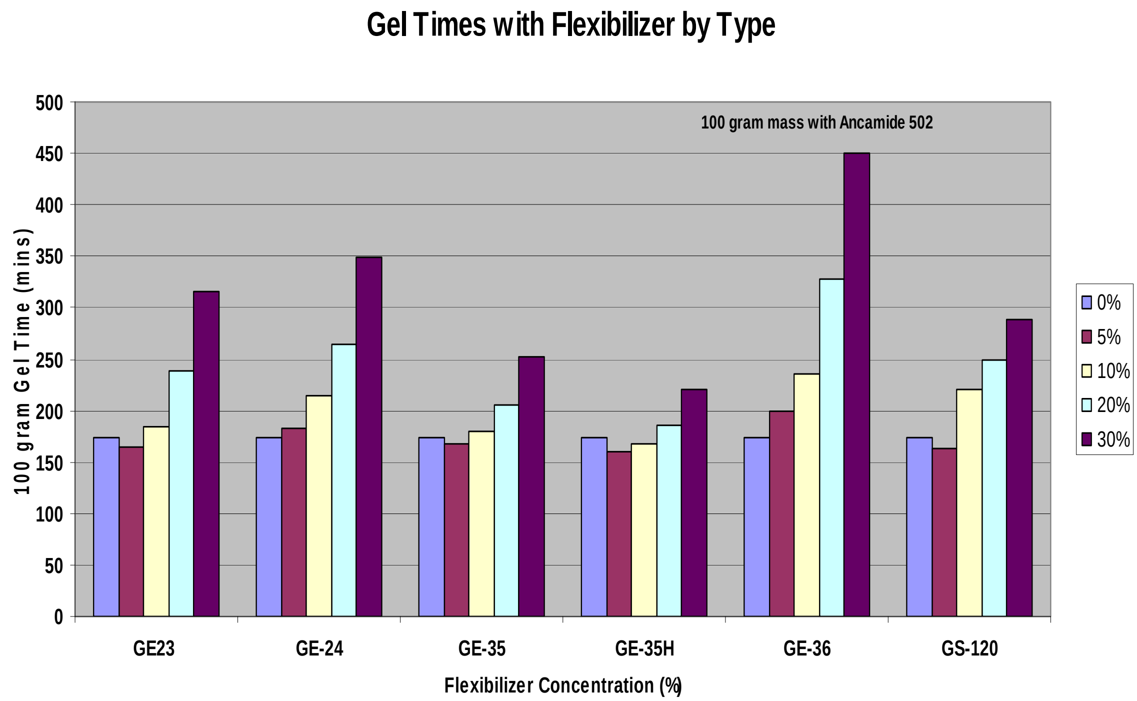
As you might expect, GE-23 modified systems show the largest effect on viscosity because it is the lowest viscosity modifier. Conversely, one would expect that GS-120, with the highest viscosity, would show the highest viscosity in formulated systems on an equal weight basis. However, this is not the case as both GE-36 and GE-35 show higher viscosity at equal levels of modification. The reason for this is not clear. The graph shown below illustrates the effect of modification on viscosity.



- Gel Time

Flexibilizing Modifiers

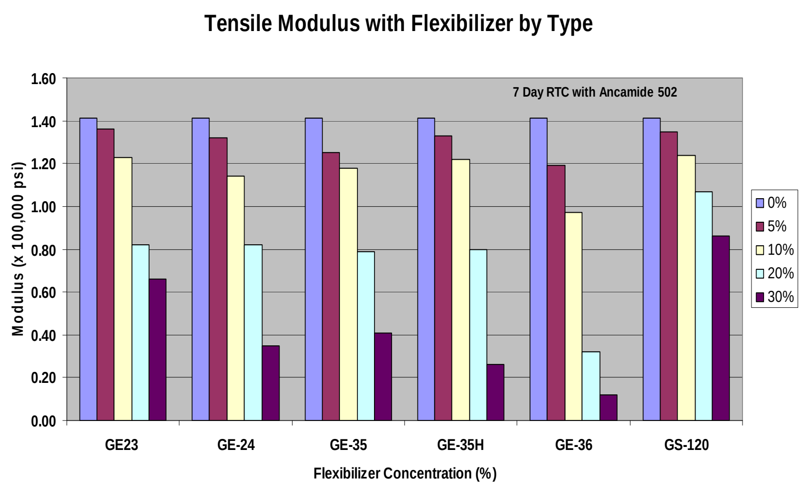
Flexibilizing modifiers tend to increase the gel time with increasing levels of use. A variety of factors can affect gel time and some of the more obvious parameters include molecular weight, equivalent weight, and functionality. Other less obvious factors can include water content, hydroxyl group content, and ionic content. As we can see in the chart below, GE35 and GE35H tend to show shorter gel times and GE-24 and GE36 tend to show longer gel times, particularly as modifier levels increase.

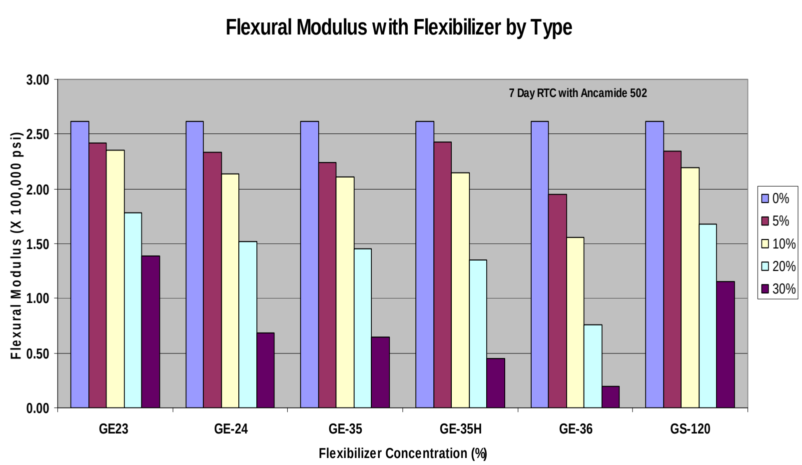


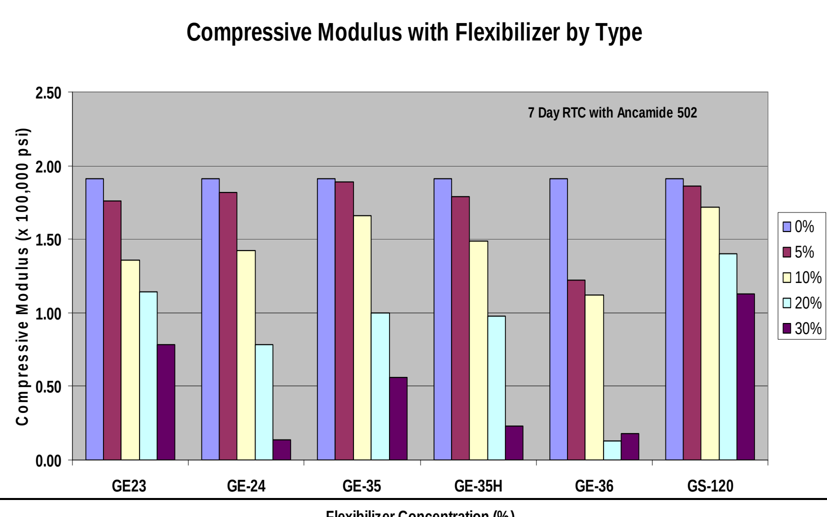
Flexibilizing Modifiers

- <u>Modulus</u>

  Modulus is a measure of the stiffness of a material. Flexibilizers will decrease the modulus of systems they are used in. In this work we looked at Tensile, Flexural, and Compressive modulus.



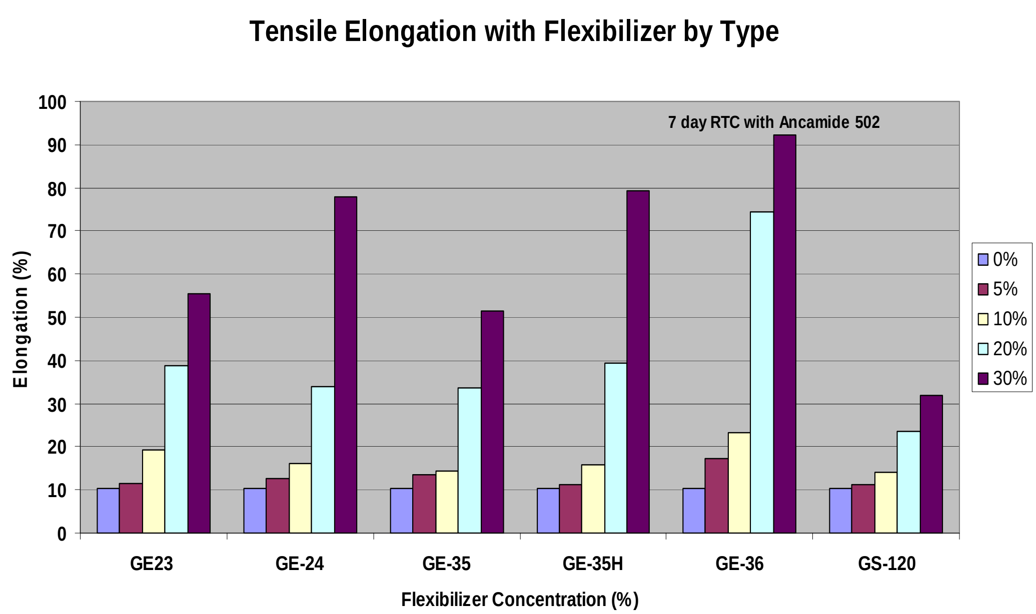




As seen in the charts above, GS120 shows, generally, higher modulus formulated systems and GE-36 shows the lower.

- Tensile Elongation

  Elongation is a key property of flexibilized systems. The chart below shows the effect of each flexiblizer on Tensile Elongation. In general, GE-36 shows the highest level of elongation and GS-120 shows the least. Given the effects shown on modulus as discussed above, this would be expected. Higher modulus materials are less flexible and lower modulus materials are more flexible.



- Temperature Resistance (Tg)

  All flexibilizing modifiers will decrease the ultimate temperature resistance of formulas in which they are used. As a general trend, one would expect those systems with higher degrees of flexibility (lower modulus) to show lower ultimate temperature resistance. However, that is not always the case. For this work we looked at the Tg of TETA cured systems. Results as shown in the table below, indicate the least effect with GE-36 which, by modulus and elongation, showed the greatest degree of flexibilization. The reason for this is that the GE-36 phase separates on cure. It also appears there may be some phase separation going on with GE-35 as well. The higher functionality of GE36 and GE35 may also be playing a role here. If Tg were measured on systems with an alternative curing agent that doesn't promote phase separation (like Ancamide 502), we would expect to see lower temperature resistance in GE36 and GE35 modified systems.

Flexibilizing Modifiers

Tg(°C) vs. % Modifier

	0%	5%	10%	20%	30%
GE-23	116	113	107	95	75
GE-24	116	108	93	77	64
GE-35	116	109	111	98	95
GE-35H	116	111	97	87	84
GE-36	116	108	106	105	102
GS-120	116	114	110	101	88
Cured with TETA; gel @ RT + 2 hours @ 100°C					

- <u>Selection Guide</u>

  As mentioned before, each modifier offers certain advantages and disadvantages. The choice of modifier should be based on which product gives the most desired balance of properties. The table below offers some guidance on where to start, suggesting a particular modifier that is best for a particular property. Complete tables of physical performance for each modifier are contained in the appendix and should be further consulted to aid choice of product.

Selection Guide

Viscosity Reduction	GE-23
Gel Time	GE-35H
Strength	GS-120, GE-23
Elongation	GE-36
High Modulus	GS-120
Low Modulus	GE-36
Temperature	Trifunctional

Appendix

Physical Properties Report	GE23 with Ancamide 502				
Epalloy 7190	100	95	90	80	70
GE-23	0	5	10	20	30
Ancamide 502	48.6	48.8	48.9	49.2	49.5
Resin Viscosity @ 25°C	12,700	6,600	3,850	1,600	800
100 gram gel time (mins)	174	165	185	239	316
Tensile Strength (psi)	7,803	7,377	6,210	3,827	3,250
Tensile Elongation (%)	10.4	11.4	19.3	38.8	55.6
Tensile Modulus (psi x 10^5)	1.41	1.36	1.23	0.82	0.66
Flexural Strength (psi)	10,370	8,815	8,558	6,416	5,317
Flexural modulus (psi x 10^5)	2.63	2.42	2.35	1.78	1.39
Compressive Yield Strength	9,511	8,022	5,716	5,102	4,033
Compressive Modulus (psi x 10^5)	1.91	1.76	1.36	1.14	0.78
Shore D Hardness	85	80	79	79	74
Water Absorption (28 days @ RT)	0.9	1.2	1.4	1.9	2.3
Water Absorption (2 hour boil)	1.1	1.0	1.3	1.5	2.0

Flexibilizing Modifiers

Physical Properties Report	GE24 with Ancamide 502				
Epalloy 7190	100	95	90	80	70
GE-24	0	5	10	20	30
Ancamide 502	48.6	47.6	46.6	44.7	42.7
Resin Viscosity @ 25°C	12,700	7,500	4,900	2,300	1,175
100 gram gel time (mins)	174	183	214	264	349
Tensile Strength (psi)	7,803	7,023	6,001	4,266	2,453
Tensile Elongation (%)	10.4	12.7	16.1	33.9	77.9
Tensile Modulus (psi x 10^5)	1.41	1.32	1.14	0.82	0.35
Flexural Strength (psi)	10,370	9,152	8,337	5,833	2,685
Flexural modulus (psi x 10^5)	2.62	2.33	2.14	1.52	0.68
Compressive Yield Strength	9,511	8,255	6,913	3,893	x
Compressive Modulus (psi x 10^5)	1.91	1.82	1.42	0.78	0.14
Shore D Hardness	85	78	72	72	63
Water Absorption (28 days @ RT)	0.9	1.2	1.5	1.9	2.5
Water Absorption (2 hour boil)	1.1	1.2	1.4	1.7	1.9

Flexibilizing Modifiers

Physical Properties Report	GE35 with Ancamide 502				
Epalloy 7190	100	95	90	80	70
GE-35	0	5	10	20	30
Ancamide 502	48.6	46.9	45.3	42.0	38.7
Resin Viscosity @ 25°C	12,700	8,300	5,900	3,500	2,250
100 gram gel time (mins)	174	168	180	205	252
Tensile Strength (psi)	7,803	6,309	6,060	3,882	2,473
Tensile Elongation (%)	10.4	13.5	14.3	33.5	51.5
Tensile Modulus (psi x 10^5)	1.41	1.25	1.18	0.79	0.41
Flexural Strength (psi)	10,370	8,772	7,794	5,495	2,503
Flexural modulus (psi x 10^5)	2.62	2.24	2.11	1.45	0.65
Compressive Yield Strength	9,511	8,545	7,587	5,089	x
Compressive Modulus (psi x 10^5)	1.91	1.89	1.66	1.00	0.56
Shore D Hardness	85	80	79	73	70
Water Absorption (28 days @ RT)	1.0	1.3	1.4	1.8	1.9
Water Absorption (2 hour boil)	1.1	1.4	1.6	1.8	1.9

Flexibilizing Modifiers

Physical Properties Report	GE35H with Ancamide 502				
Epalloy 7190	100	95	90	80	70
GE-35H	0	5	10	20	30
Ancamide 502	48.6	47.7	45.2	41.8	38.3
Resin Viscosity @ 25°C	12,700	7,900	5,500	3,200	1,400
100 gram gel time (mins)	174	160	167	186	220
Tensile Strength (psi)	7,803	7,187	6,367	3,934	2,126
Tensile Elongation (%)	10.4	11.2	15.7	39.3	79.3
Tensile Modulus (psi x 10^5)	1.41	1.33	1.22	0.80	0.26
Flexural Strength (psi)	10,370	9,158	8,077	5,098	1,723
Flexural modulus (psi x 10^5)	2.62	2.43	2.15	1.35	0.45
Compressive Yield Strength	9,511	8,700	7,200	4,477	x
Compressive Modulus (psi x 10^5)	1.91	1.79	1.49	0.98	0.23
Shore D Hardness	85	81	75	75	68
Water Absorption (28 days @ RT)	0.9	1.2	1.4	1.8	2.1
Water Absorption (2 hour boil)	1.0	1.5	1.7	1.8	2.2

Flexibilizing Modifiers

Physical Properties Report	**GE-36 with Ancamide 502**				
Epalloy 7190	100	95	90	80	70
GE-36	0	5	10	20	30
Ancamide 502	49.5	47.7	45.9	42.3	38.7
Resin Viscosity @ 25°C	12,700	8,000	6,200	3,500	2,300
100 gram gel time (mins)	174	200	235	328	450
Tensile Strength (psi)	7,803	6,023	4,767	1,879	1,283
Tensile Elongation (%)	10.4	17.3	23.4	74.3	92.3
Tensile Modulus (psi x 10^5)	1.41	1.19	0.97	0.32	0.12
Flexural Strength (psi)	10,370	7,512	6,341	1,367	597
flexural modulus (psi x 10^5)	2.62	1.95	1.56	0.76	0.20
Compressive Yield Strength	9,511	6,626	5,598	x	x
Compressive Modulus (psi x 10^5)	1.91	1.22	1.12	0.13	0.18
Shore D Hardness	85	80	79	70	59
Water Absorption (28 days @ RT)	0.9				
Water Absorption (2 hour boil)	1.1	1.2	1.5	2	2.2

Flexibilizing Modifiers

Physical Properties Report	GS-120 with Ancamide 502				
Epalloy 7190	100	95	90	80	70
GS-120	0	5	10	20	30
Ancamide 502	48.6	47.3	46.0	43.3	40.7
Resin Viscosity @ 25°C	12,700	7,800	5,500	3,200	2,000
100 gram gel time (mins)	174	163	220	250	288
Tensile Strength (psi)	7,803	7,437	6,932	5,751	4,652
Tensile Elongation (%)	10.4	11.2	14.1	23.6	31.9
Tensile Modulus (psi x 10^5)	1.41	1.35	1.24	1.07	0.86
Flexural Strength (psi)	10,370	9,381	8,700	6,620	4,834
Flexural modulus (psi x 10^5)	2.62	2.34	2.19	1.68	1.15
Compressive Yield Strength	9,511	8,928	8,196	6,797	5,197
Compressive Modulus (psi x 10^5)	1.91	1.86	1.72	1.40	1.13
Shore D Hardness	85	82	80	76	63
Water Absorption (28 days @ RT)	0.9	1.3	1.5	1.9	2.2
Water Absorption (2 hour boil)	1.1	1.2	1.5	1.8	2.0