Hypro™ 1300X16 ATBN in Elastomeric Epoxies

Introduction:

Hypro reactive liquid polymers (RLP) are recognized as tougheners for thermoset resins specifically of the epoxy variety. In such formulations these CTBN or ATBN liquid polymers typically would be used at a level of 10-20 phr (parts per hundred resin). The stress-strain properties associated with elastomer toughened epoxies don't differ appreciably from that of an unmodified epoxy resin although its tensile elongation might be somewhat greater. The defining property for an elastomer toughened epoxy is enhanced fracture surface energy. This bulletin does not address elastomer toughened epoxy resins.

A departure from the use of RLP as tougheners is in highly flexible epoxy compositions and the scope of this TSR. In particular Hypro™ 1300X16 ATBN was examined in 2-part epoxy resins to achieve mechanical properties necessary for crack bridging coatings or moisture resistant membranes. Additionally, it was compared to a blocked urethane polymer (Desmocap 12A) commonly considered by epoxy formulators in designing flexible, 2-component epoxy resins for civil engineering-construction applications as crack bridging coatings, membranes, sealants, etc.

Formulations/Results

Initially an arbitrary rubber (ATBN) level of 100 phr was chosen to characterize low modulus-high elongation epoxy compositions. The curing agent was Ancamine 2072, a phenol-free, cycloaliphatic amine. The study included Desmocap 12A. The recipes follow in which ATBN and Desmocap 12A were used alone in A and E, respectively with the other recipes using combinations of these two flexibilizers-again noting that epoxy technologists usually don't think about the flexibilization possibilities with reactive liquid polymers.

Recipe	A	B	C	D	E
Epalloy 7190	100	100	100	100	100
Desmocap 12A	0	25	50	75	100
ATBN 1300X16	100	75	50	25	0
Ancamine 2072	42.4	46.9	51.4	56	60.5
Mix viscosity, mPa.s	14,700	14,600	9,450	7,540	6,220
Cure- 7 days at R.T.					
Tensile strength, MPa	19.4	16.6	16.8	14.8	13.2
Tensile elongation, %	124	98	105	94	86
Tensile modulus, GPa	0.717	0.681	0.573	0.387	0.321

The ATBN modified epoxy has a better balance of mechanical properties than Desmocap 12A modified epoxy comparing recipe A to recipe E. The ATBN/Desmocap 12A blends have intermediate elongations, tensile strengths and tensile modulus.

Low temperature properties were measured as well. Thus stress-strain properties at -20˚C were determined after the same cure schedule as above.

Tensile strength, MPa	39.7	37.2	39.6	33.5	29.4
Tensile elongation, %	109	84	95	80	70
Tensile modulus, GPa	2.29	1.11	0.965	0.724	0.606

The ATBN modified epoxy formulation appeared to have greater integrity than the Desmocap modified epoxy formulation based on a stress-strain criterion alone. However the chemical resistance aspect of the urethane (Desmocap) modified epoxy and nitrile (ATBN) rubber modified epoxy systems as illustrated in the next section is more differentiating in performance.

Chemical Resistance of ATBN and Desmocap Modified Epoxy Resins

Sometime ago there was a considerable amount of industry-wide effort in an area known as secondary containment coatings. These are 10-40 mils thick coatings used to protect underlying concrete substrate from hazardous, chemical spills. With that in mind, an amine hardener (Ancamine 2280) was chosen for its excellent chemical resistance. Additionally, a phenol novolac epoxy resin having an average epoxy functionality of 2.6 was used to provide greater chemical resistance than a bisphenol A epoxy resin. A small amount of a glycol diepoxide (Erisys™ GE-23) was used to lower mix viscosity.

Similarly to the above compositions 1300X16 ATBN was formulated at a 100 phr level-see recipe F. Unlike the previous recipes a non-flexibilized control was compared to ATBN and ATBN/Desmocap 12A modified resins. Formulations and stress strain properties follow:

Recipe	F	G	H
Epalloy 8250	90	90	90
Erisys GE-23	10	10	10
Desmocap 12A	0	0	50
ATBN 1300X16	100	0	50
Ancamine 2280	50.1	62.2	60.7
Cure, 7 days at R.T.			
R.T. Properties			
Tensile strength, MPa	14.8	30.4	14.1
Tensile elongation,%	48	9.1	74
-20C Properties			
Tensile strength, MPa	28.5	59.8	27.8
Tensile elongation, %	38	3.4	64

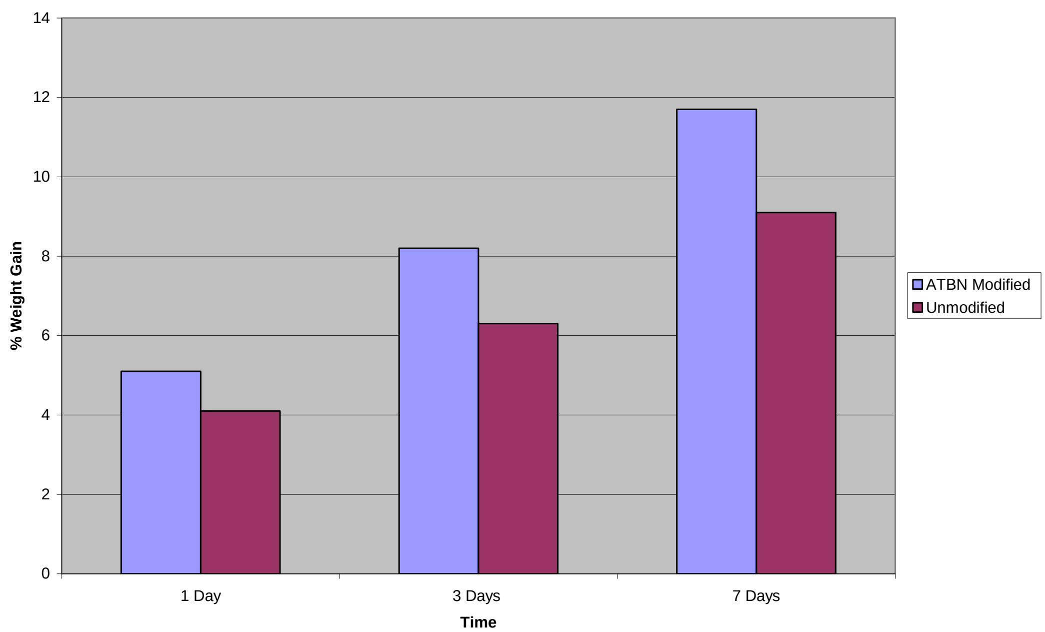
Recipes F-H represent more highly cross linked epoxy resins than recipes A-E due to influence of Epalloy™ 8250. That has an appreciable effect on tensile elongation with the ATBN flexibilized bisphenol A epoxy having a tensile elongation in excess of 100% and an ATBN flexibilized phenol novolac epoxy having a tensile elongation of 50%: An implication of those properties is that the former might have better crack bridging capability than the latter. Conversely the latter would have better chemical resistance leading to the next section.

Organic and inorganic chemical resistance was determined for the ATBN and ATBN/Desmocap 12A containing epoxy systems by immersing the plaques in 1) 25% acetic acid, 2) 45% nitric acid and 3) 98% sulfuric acid for up to 7 days and measuring weight gain (loss).

ATBN modified epoxy (recipe F) compared quite favorably to the unmodified control regarding acetic acid resistance. See Figure 1.

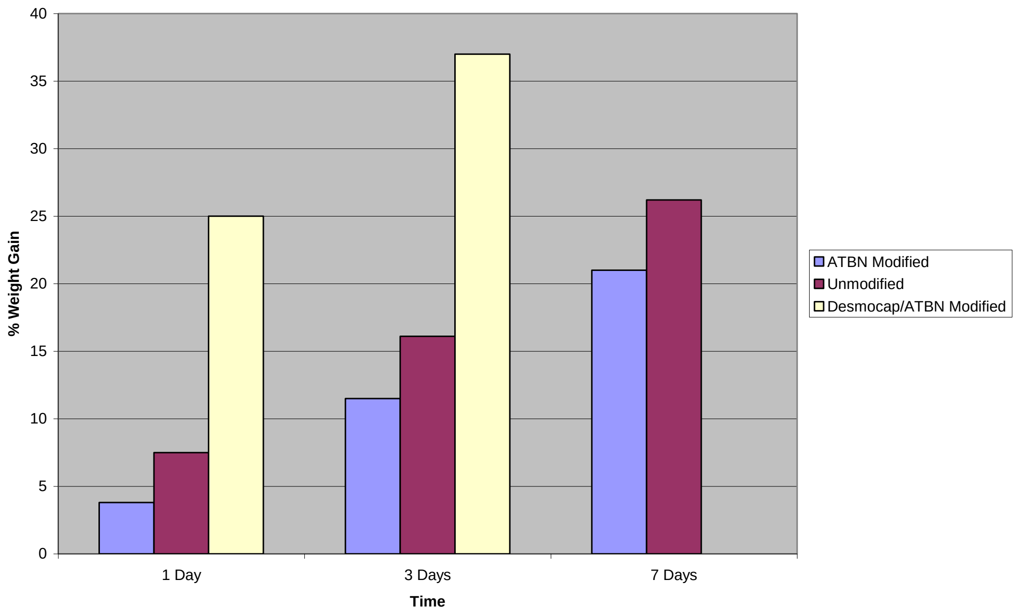
Remarks: Data for the Desmocap/ATBN modified epoxy are not provided in Figure 1 as the plaque had neither a weight gain nor a weight loss-it was destroyed after 1 day of immersion.

Figure 1-Weight Gain After Immersion in 25% Acetic Acid



The ATBN modified epoxy (recipe F) performed as well if not slightly better than the unmodified control in a 45% nitric acid environment. The Desmocap/ATBN modified epoxy was significantly worse than the ATBN modified system with testing discontinued after 3 days based on its large weight gain-See Figure 2.

Figure 2- Weight Gain After Immersion in 45% Nitric Acid



The flexibilized epoxy resins were exposed to 98% sulfuric acid with both recipes G and H destroyed after two days. The unmodified control had a 2.4% weight loss. Undoubtedly, a lower rubber (ATBN) level than 100 phr would be recommended to achieve enhanced concentrated sulfuric acid resistance.

Adhesives Data

Another study was conducted in which 1300X16 ATBN was compared to Desmocap 12A in an amidoamine cured epoxy resin. 1300X16 ATBN and Desmocap were examined at lower levels than in the previous work. Therefore modifier concentrations of 25 and 50 phr represented by recipes L-M certainly are more typical of the use of ATBN in epoxy applications as structural and semi-structural adhesives. An elastomer (ATBN) modified epoxy adhesive has greater peel strength than a urethane (Desmocap 12A) modified epoxy adhesive on cold rolled and electro galvanized steel substrates.

Recipe	I	J	K	L	M
Epalloy 7190	100	100	100	100	100
Tabular Alumina	40	40	40	40	40
Desmocap 12A	0	25	50	0	0
ATBN 1300X16	0	0	0	25	50
Ancamide 501	35	36.9	38.9	33.1	31.3
Cure: 1 hour @ 125C					
Substrate-cold rolled steel					
Lap shear strength, MPa	5.17	8.34	8.62	10.21	9.45
T-Peel strength, N/mm.	0.91	1.9	1.81	2.94	2.47
Electro galvanized steel					
Lap shear strength, MPa	5.63	7.86	10.43	9.96	8.21
T-Peel strength, N/mm	1.2	2.11	2.13	2.7	2.99

Conclusions:

1) ATBN reactive liquid polymers may be considered as epoxy flexbilizers in addition to their traditional use as tougheners.
2) As such ATBN compares more than favorably to Desmocap 12A in terms of mechanical properties and aqueous organic and inorganic resistance.
3) Beyond the flexibilization aspect of these amine terminated butadiene-acrylonitrile copolymers, elastomeric epoxies can be designed by incorporating stoichiometric levels of ATBN in a liquid epoxy containing formulation.