

Hypro™ RLP and HyPox™ CTBN Modified Epoxies in 1- and 2- Part Adhesives

Introduction:

There are two principal approaches to modifying one- and two-part component amine cured epoxy resins with Hypro reactive liquid polymers which are 1) ATBN added to amine hardener side and 2) HyPox CTBN/epoxy adducts added to the resin side. This document contains adhesives data based on elastomer modified epoxies employing these formulating concepts. Additionally, there are some nuances associated with rubber modified epoxy resins that are illustrated by select formulations.

Two-Part Adhesives

Hypro 1300X16 ATBN was examined at a 30 phr (parts per hundred resin) level in two polyamide cured epoxy adhesive recipes. The elastomer modified adhesives were significantly tougher than the unmodified adhesives evidenced by the generous increase in T-Peel strength. Lap shear strength measured at -40°C and room temperature was greater as well for the rubber modified versions. Elevated temperature lap shear strength for the ATBN modified adhesives was lower than that for the control which can be explained due to lowering of the epoxy TG due to the high rubber level.

	Unmodified		Elastomer Modified	
	1	2	3	4
EPALLOY™ 7190	100	100	100	100
Atomite Whiting	30	30	30	30
Ancamide 350A	60	-	56.4	-
Ancamide 400	-	50	0	46.8
Hypro™ 1300X16 ATBN	-	-	30	30

Substrate: Sandblasted Cold Rolled Steel

Cure: Two weeks at room temperature

Lap Shear, psi				
-40°C	1,370	1,440	2,260	2,288
R.T.	1,600	1,508	2,508	2,540
83°C	2,088	2,188	1,575	1,484

T-Peel, pli				
R.T.	3.3	3.0	35.0	31.0

Atomite Whiting – Calcium Carbonate (Filler), Ancamide 350A/400 – Fatty Polyamide (Curing Agent)

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Two-Part Adhesives

It is a common practice to use more than one type of amine hardener in two-part epoxy resins. The following model recipe is such an example where a modified aliphatic amine and fatty polyamide served as co-hardeners. The rubber level used in recipes 2-4 was 25 phr noting that in the case of recipes 3 and 4 rubber was introduced in the form of HyPox™ RA840 and RA1340. (Both RA840 and RA1340 are 40% by weight CTBN rubber concentrates).

The T-peel results suggest that in this particular system, HyPox RA840 or RA1340 is more effective than Hypro™ 1300X16 ATBN although it also gave superior peel strength to that of the unmodified, control.

	1	2	3	4
EPALLOY 7190 (EEW-190)	100	100	62.5	62.5
Hypro 1300X16 ATBN	-	25	-	-
HyPox RA840 ¹	-	-	62.5	-
HyPox RA1340 ²	-	-	-	62.5
Aliphatic Amine Adduct ²	28.2	25.4	27.4	27.4
Polyamide ⁴	26.3	23.7	25.6	25.6
Filler (Tabular Alumina)	40	40	40	40
Rubber Concentration,phr	0	25	25	25

Cure: 1 hour@ 125°C

Substrate: Cold Rolled Steel

	1	2	3	4
Lap Shear, MPa (Psi)	4.8 (700)	11.0 (1590)	11.3 (1640)	13.1 (1900)
T-peel, kg/cm (Pli)	0.9 (4.9)	2.2 (12.3)	2.9 (16.4)	6.0 (33.3)

Substrate: Electrogalvanized Steel

	1	2	3	4
Lap Shear, MPa (Psi)	3.5 (505)	13.2 (1920)	11.4 (1660)	8.1 (1180)
T-peel, kg/cm (Pli)	0.8 (4.3)	2.9 (16.5)	3.3 (18.2)	430 (24.3)

¹ Epoxy/CTBN Adduct; 60% epoxy; 40% CTBNX8

² Epoxy/CTBN Adduct; 60% epoxy, 40% CTBNX13 (EEW-340)

³ Ancamine AD, Equivalent Weight (Weight per active Hydrogen) – 107

⁴ Ancamide 350A, Equivalent Weight (Weight per active Hydrogen) – 100

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The previous two-part epoxy adhesives were given an elevated temperature cure as the intent of that study was to maximize adhesive performance. In the following two-part epoxy formulation a room temperature cure was used. In addition, the recipe contained only one amine hardener and a nuance to rubber modification previously referred to is demonstrated in the composition.

Hypro 1300X16 ATBN did not respond favorably as a toughener and that is due to the fact that it, as well as other grades of ATBN, is extremely incompatible with aliphatic amines. Not only does ATBN phase separate in such rubber/amine blends but in a fast reacting system as an aliphatic amine cured epoxy, the slower reacting ATBN does not have a chance to react with the epoxy. However, an epoxy/CTBN adduct performs quite well in aliphatic amine/epoxy systems with T-peel strength supporting that claim.

In this specific case HyPox RA1340, based on a CTBN having higher acrylonitrile content than HyPox RA 840, was the better toughener. However, in another amine cured epoxy formulation, the reverse could be true – indicating that formulators should investigate both HyPox RA840 and RA1340 in amine cured epoxy systems. Further considerations should be made to examine other CTBN/epoxy adducts as those featuring epoxy phenolic novolac resins, Bisphenol F resins, etc.

	Unmodified	Elastomer Modified		
EPALLOY 7190	100	100	77.5	77.5
Atomite Whiting	30	30	30	30
Ancamine AD ¹	60	58.2	59.3	59.3
Hypro 1300X16 ATBN	--	15	--	--
HyPox RA840 ²	--	--	37.5	--
HyPox RA1340	--	--	--	37.5

Substrate: Sandblasted Cold Rolled Steel

Cure: Two weeks at R.T.

Lap Shear, psi		Hypro 1300X16 ATBN	Hypro 1300X8 CTBN	Hypro 1300X13 CTBN
40°C	1000	1200	3500	1500
R.T.	1200	2500	2700	2500
83°C	<100	<100	<100	<100

T-Peel, pli				
R.T.	<5	<5	28	12

¹ Ancamine AD – Aliphatic Amine Adduct (Hardener)

² HyPox RA840 is a CTBN-Epoxy adduct made with 60% epoxy, 40% Hypro CTBNX8 by weight (EEW=30)

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One-Component Paste Adhesives

The final set of recipes/data is a model one-part epoxy paste adhesive of the substituted urea accelerated dicyandiamide cured variety. By virtue of the oily substrates a potential market for these rubber toughened epoxy adhesives is automotive adhesives.

Typically a higher cure temperature will provide better mechanical properties in epoxy resins and elastomer toughened epoxy adhesives are no exception. Therefore, enhanced peel strength was achieved with the 204°C (400°F) cure compared to the 121°C (250°F) cure.

Unmodified	Elastomer Modified
EPALLOY 7190 – 100	EPALLOY 7190 – 77.5
Tabular Alumina – 40	Tabular Alumina - 40
Cab-O-Sil N70-TS – 3.5	Cab-O-Sil N70-TS – 3.5
OMICURE DDA10 – 6.0	OMICURE DDA10 – 6.0
OMICURE U405 – 2.0	OMICURE U405 – 2.0
	CTBN/Epoxy Adduct – 37.5

Substrate: Oil Contaminated Hot Dipped Galvanized

Cure: 1 Hour at 250°F

		Hypro 1300X8 CTBN	Hypro 1300X13 CTBN
Lap Shear, psi	1880	2980	3340
T-Peel, pli	4.6	22.3	28.2

Cure: 20 Minutes at 400°F

Lap Shear, psi	2800	2810	3580
T-Peel, pli	8.5	44.6	53.6

EPALLOY 7190 – Diglycidyl ether of Bisphenol A (epoxy), Tabular Alumina – aluminum oxide (filler), Cab-O-Sil, N70-TS, fumed silica (thixotrope), OMICURE DDA 10 – latent hardener, Omicure U-405 – substituted urea (accelerator)