Reactive Liquid Polymer Modified Epoxy Powder Coatings

Introduction; -- Reactive liquid polymers commonly used in the thermoset resin industry are carboxyl terminated butadiene-acrylonitrile (CTBN) copolymers. In a continuous epoxy matrix CTBN will form a discontinuous secondary phase resulting in an elastomer toughened thermoset epoxy.[1,2] A considerable amount of research has taken place in academia and industry over the years in the area of elastomer toughened thermoset resins designed for structural applications. The use of CTBN's in coatings applications has been studied to a lesser degree[3-7]; and in powder coatings, even less. The scope of this project was to examine different grades of CTBN in two model formulations representing epoxy powder coatings for high performance, functional applications.

CTBN is a low molecular weight, random butadiene-acrylonitrile copolymer having carboxyl acid termination. Various grades of CTBN differ in bound acrylonitrile content as illustrated in the product summary found in Table 1.

Table 1 – Properties of CTBN Grades used in Study

	Hypro 1300X31 CTBN	Hypro 1300X8 CTBN	Hypro 1300X9 CTBNX	Hypro 1300X13 CTBN
Acrylonitrile Content (%)	10	18	18	26
Acid number	28	29	38	32
EPHR*	0.050	0.052	0.067	0.057
Viscosity (cP @ 27°C)	60,000	135,000	160,000	500,000
Molecular Weight (M_n)	3800	3550	3600	3150
Tg (°C)**	-66	-52	-52	-39

* EPHR is Equivalents per hundred rubber; ** measured via DSC

The intermediate to high acrylonitrile containing liquid polymers are usually preferred to the lower acrylonitrile containing versions for epoxy modification due to their better inherent compatibility with epoxy resin. As an example Hypro 1300X13 CTBN is an excellent toughener for dicyandiamide cured epoxy resins often used as structural adhesives. On that knowledge basis, Hypro 1300X8 CTBN and Hypro 1300X13 CTBN were investigated as tougheners for epoxy powder coatings. Additionally, other commercial CTBN resins with lower acrylonitrile content were examined. These included Hypro 1300X31 CTBN (10%

acrylonitrile) and Hypro 1300X9 CTBNX (18% acrylonitrile), which also contains added pendant carboxyl functionality. Therefore it was a thorough study aimed at determining the merit of elastomer toughened epoxy powder coatings featuring several grades of CTBN.

Experimental -- The CTBN polymers under study in this work are rather viscous liquids. At typical toughener levels of 10-15 phr (parts per hundred), it would not be practical to use them as modifiers for a powder coating formulation. Instead, it was decided to manufacture solid resin based adducts by chemically reacting the carboxylic acid of the CTBN's with the epoxy groups on the resin. This reaction, known as addition esterification, is routinely practiced by those preparing CTBN elastomer toughened epoxies. The epoxy resins used in this study were Epon® 2004, a solid bisphenol A/epichlorohydrin epoxy having an Epoxy Equivalent Weight (EEW) of 875-975 and Epon 2014, a solid bisphenol A/epichlorohydrin epoxy, blended with an epoxy novolac resin, having an EEW of 750 to 850.

All CTBN liquid polymers were pre-polymerized or adducted with the epoxy prior to powder processing in the extruder. Reaction conditions were 3-4 hours at 170°C without catalyst. Epoxy resin and CTBN were reacted to an acid number of less than 1 at which time the reaction was considered complete. The rubber level in the epoxy adducts was 13% by weight, based on a CTBN concentration of 15 phr (parts per hundred resin).

Other formulating ingredients used in preparing the elastomer modified epoxy powder coatings included curing agent, filler and flow control agent. The cross linker used with Epon 2004 was Epikure® P-104, an accelerated dicyandiamide hardener. The cross linker used with Epon 2014 was Epikure® P-202, a 2-methylimidazole containing phenolic hardener. Predominate filler employed was barium sulfate with calcium carbonate used in a couple of systems. Tables 2 & 3 show the elastomer modified epoxy powder coating recipes used.

Table 2 – Model Recipes for Powder Coatings Formulation based on Epon 2004

	A	B	C	D	E	F	G
Epon 2004	100	0	100	0	0	0	0
X8 Adduct	0	100	0	100	0	0	0
X31 Adduct	0	0	0	0	100	0	0
X9 Adduct	0	0	0	0	0	100	0
X13 Adduct	0	0	0	0	0	0	100
Epikure P-104	4	3.5	4	3.5	3.5	3.5	3.5
Barium Sulfate	35	35	0	0	35	35	35
Calcium Carbonate	0	0	21.3	21.3	0	0	0
Modaflow	1.4	1.4	1.4	1.4	1.4	1.4	1.4

Table 3 – Model Recipes for Powder Coatings Formulation based on Epon 2014

	I	J	K	L	M	N	O
Epon 2014	100	0	100	0	0	0	0
X8 Adduct	0	100	0	100	0	0	0
X31 Adduct	0	0	0	0	100	0	0
X9 Adduct	0	0	0	0	0	100	0
X13 Adduct	0	0	0	0	0	0	100
Epikure P-202	25.4	22.1	25.4	22.1	22.1	22.1	22.1
Barium Sulfate	42.3	42.3	0	0	42.3	42.3	42.3
Calcium Carbonate	0	0	25.7	25.7	0	0	0
Modaflow	1.4	1.4	1.4	1.4	1.4	1.4	1.4

Initially, clear powder coating formulations were prepared as a screening tool for further work. For that part of the project only Hycar 1300X8 CTBN and Hycar 1300X13 CTBN containing adduct formulations were evaluated. The model formulations shown in Tables 2 and 3 without filler were used. Gardner impact (direct and reverse falling dart) was measured on 10 -12 mil films on iron phosphate treated steel substrate (1000 Bonderite panels).

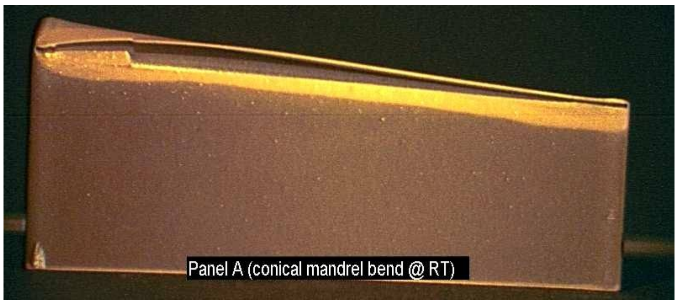
Results (Table 4) indicate CTBN's 1300X8 and 1300X13 at 15 phr rubber levels both increased significantly the impact strength of the Epon 2014 based clear coatings. 1300X13 was also very effective with the Epon 2004 based coating while 1300X8 was somewhat less effective. Furthermore, morphology was examined to determine the presence of a second phase. Rubber particles were not detected by SEM (scanning electron microscopy).

Table 4 – Gardner Impact on Unfilled CTBN Modified Epoxy Powder Coatings

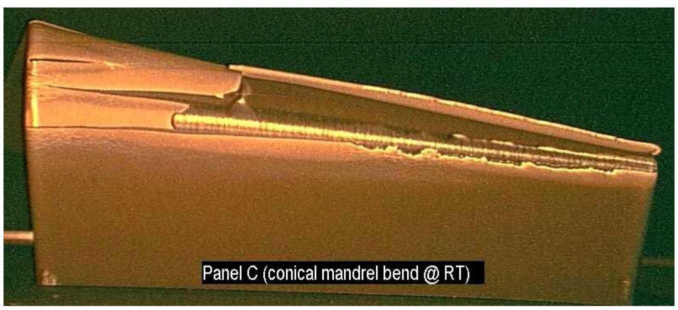
Coating	Impact, in-lbs. (Direct/Reverse)
Epon 2004/P104	
Unmodified	40/40
CTBN1300X8 modified	160/60
CTBN1300X13 modified	160/160
Epon 2014/P202	
Unmodified	60/40
CTBN1300X8 modified	160/160
CTBN1300X13 modified	160/160

The promising results obtained with unfilled coatings led to further work to evaluate impact and flexibility in the filled powder coating compositions shown in Tables 2 and 3. As mentioned previously, Gardner Impact (falling dart) was used to measure impact strength and 1/8” conical mandrel bend was used to evaluate flexibility. The filler was barium sulfate in most compositions and calcium carbonate in others. In all cases the PVC (pigment volume concentration) was 8.4%. Curing agent levels were adjusted based on the EEW (Epoxy Equivalent Weight) for the resin components used. Modified formulas used lower amounts of catalyst due to the higher EEW of the adduct components.

The conical mandrel bend test was quite useful in terms of separating the performance of flexibilized coatings from non-flexibilized coatings. Coated panels were bent over an 1/8 inch conical mandrel at room temperature (R.T.) and then examined for film integrity. Photographs of each of the unmodified formulations (A, C, I, & K) following mandrel bend are shown as follows. All cracked upon bending over the 1/8 inch mandrel.

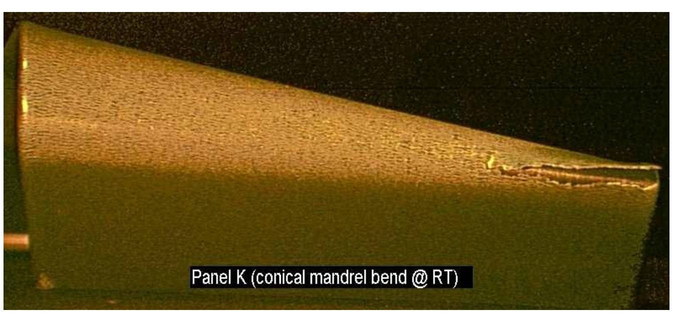


Recipe A -- Unmodified Epon 2004 w/ $BaSO_4$ Filler



Recipe C -- Unmodified Epon 2004 w/$CaCO_3$ Filler

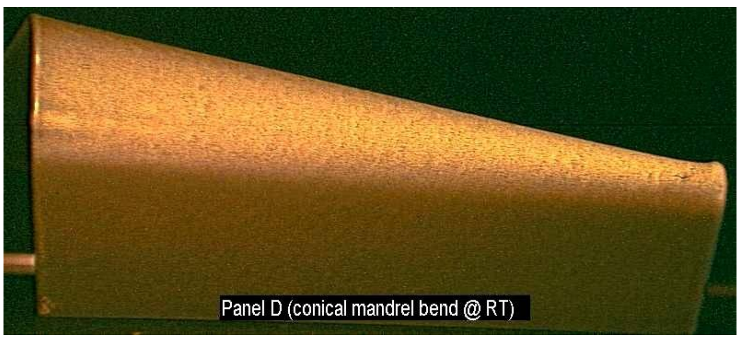
Recipe I -- Unmodified Epon 2014 w/ $BaSO_4$ Filler



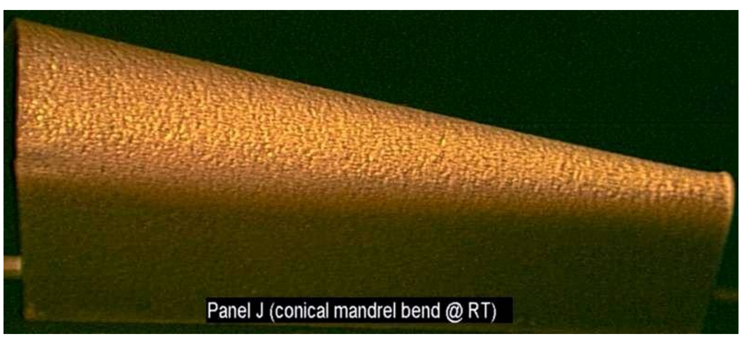
Recipe K -- Unmodified Epon 2014 w/$CaCO_3$ Filler

The CTBN modified resins (B,D,J,& L) showed great improvement in flexibility as measured by conical mandrel bend with either no or very slight cracking observed.

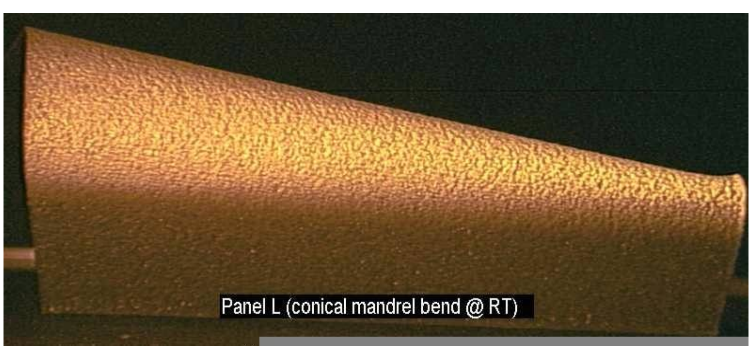
Recipe B -- CTBNX8 modified Epon 2004 w/$BaSO_4$ Filler



Recipe D -- CTBNX8 modified Epon 2004 w/ $CaCO_3$ Filler



Recipe J -- CTBNX8 modified Epon 2014 w/$BaSO_4$ Filler



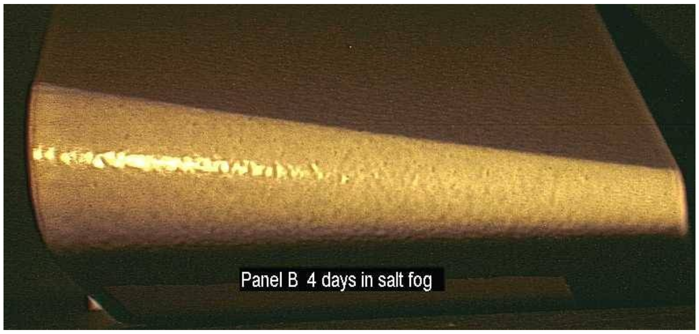
Recipe L -- CTBNX8 modified Epon 2014 w/ $CaCO_3$ Filler

Although not shown here, similar favorable results were seen in conical mandrel bend tests for formulations E, F, G, M, N, & O, which are powder formulations made with adducts of CTBNX31, X9, and X13 with Epon 2004 and Epon 2014.

Reactive Liquid Polymer Modified Epoxy Powder Coatings

The mandrel bend test highlights the brittle nature of the unmodified coatings. Subsequently some of the bent panels were exposed to a 5% salt fog environment for several days for corrosion testing. Considerable corrosion of the steel was observed for the unmodified coated panels whereas the metal featuring the elastomer modified epoxy powder coatings exhibited no corrosion. Comparison photographs are shown below.

Unmodified Epon 2004 w/$BaSO_4$ Filler



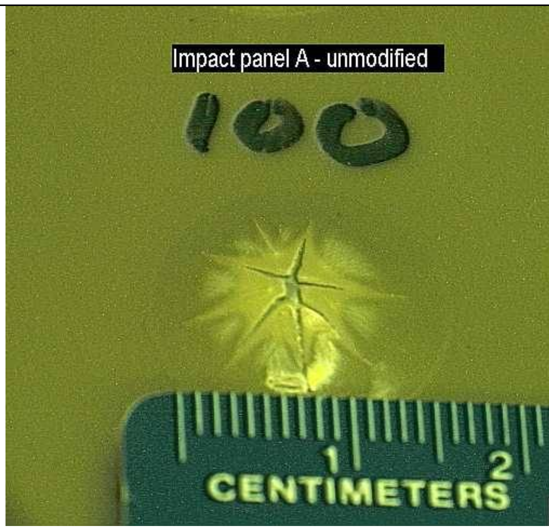
CTBNX8 modified Epon 2004 w/$BaSO_4$ Filler

Unmodified Epon 2004 w/$CaCO_3$ Filler

CTBNX8 modified Epon 2004 w/ $CaCO_3$ Filler

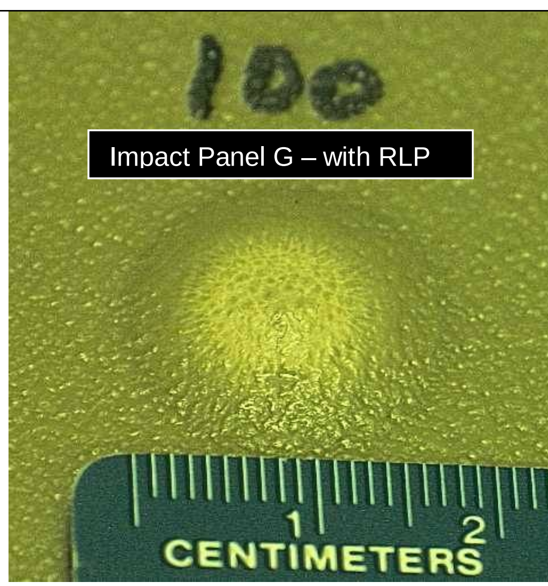
Reactive Liquid Polymer Modified Epoxy Powder Coatings

Reverse impact was determined to be a more discriminating test to evaluate differences between the coatings tested. Favorable results were observed with the elastomer modified coatings. For instance formula B (featuring 1300X8 CTBN/Epon 2004) maintained its film integrity after 100 in-lbs reverse impact whereas the coating associated with unmodified recipe A, was punctured. Likewise, modified formulation G (featuring 1300X13 CTBN/Epon 2004) showed excellent impact resistance under the same test conditions.



Formula A – Unmodified Epon 2004

Formula B – 1300X8 CTBN Modified Epon 2004



Formula G – 1300X13 CTBN Modified Epon 2004

Reactive Liquid Polymer Modified Epoxy Powder Coatings

Discussion and Conclusions -- Hypro Carboxy Terminated Butadiene Nitrile (CTBN) reactive liquid polymers may be used to modify epoxy powder coatings by reacting a CTBN liquid polymer with a solid epoxy to form the base resin. Although it is not fully understood as to whether the toughening or flexibilizing mechanism may be operating based on the work done in this study, the elastomer modified epoxy powder coatings appear to be more durable than the unmodified coatings. The commercially available Hypro CTBN's (1300X8, 1300X9, 1300X13, or 1300X31) can be converted into suitable epoxy adducts and evaluated as the base resin in functional epoxy powder coatings. Alternatively, a commercial source for a CTBN1300X13 modified solid resin is available in the form of HyPox RK84L. This product could potentially be blended into a commercially available solid resin product, along with fillers, pigments, flow control agents, and curing agents, and evaluated for use as a powder coating resin.

References:

1. D.L. Hunston and W.D. Bascom, Failure Behavior of Rubber-Toughened Epoxies in Bulk, Adhesive, and Composite Geometries, Advances in Chemistry Series 208 (1984)

2. A.J. Kinloch, Relationships Between the Microstructure and Fracture Behavior of Rubber-Toughened Thermosetting Polymers, Advances in Chemistry Series 222 (1989)

3. U.S. Patent 4,804,581; PPG

4. U.S. Patent 5,008,334; BASF

5. U.S. Patent 5,248,400; PPG

6. U.S. Patent 5,264,503; Shell

7. U.S. Patent 4,921,913; PPG