New CTBN/Epoxy Adduct Technology

Background

Emerald Performance Materials has developed new, patent pending, technology in reactive liquid polymers (RLP) epoxy adduct syntheses. These adducts do not separate when diluted with standard DGEBA (diglycidyl ether of bisphenol A) resins and, when formulated into an adhesive, provide excellent low temperature properties. Typical adducts of Hypro™ 1300X8 CTBN and 1300X13 CTBN give good room temperature performance but the low temperature performance is typically lacking. Adducts of Hypro 2000X162 CTB give good low temperature performance, but the rubber portion separates upon aging. The new technology combines the good room temperature performance of CTBN with improved low temperature properties due to the presence of CTB in the adduct. CTB has the lowest Tg (glass transition temperature) in the RLP product line.

Adduct synthesis

These new adducts are obtained using a combination of a CTBN with high bound acrylonitrile content in combination with a CTB(N) with low or no bound acrylonitrile. The best results are obtained when CTB (Carboxyl Terminated Butadiene) is used. The synthesis involves first mixing CTBN (typically 1300X13) with CTB and then adding DGEBA (EEW ~190) so that there are approximately 2 epoxy units to every carboxyl group. Reaction proceeds until almost all the acid has been consumed. The following examples are indicative of the process with **Table 1** containing a recipe for making this unique adduct.

Table 1

CAS #	Chemical Name	Ephr[1]	Wt (g)
68891-46-3	1300X13 CTBN (27% wt of nitrile)	0.058	145.0
68891-79-2	2000X162 CTB (0% wt of nitrile)	0.043	145.0
25068-38-6	Epon 828		57.1

[1]Equivalents per hundred resin

Procedure:

All ingredients were weighed in a 1 liter, three-neck mechanically stirred flask equipped with a nitrogen inlet and outlet. The ratio of epoxide functionality to carboxyl functionality was 2 to 1.The ingredients were heated to 120°C under slow nitrogen purge. The reaction required four hours to reach the ≤0.001 Ephr endpoint. The finished product was an opaque viscous liquid. To test the compatibility of this resin it was further diluted in Epon 828. 18 grams of the adduct were dissolved in 97 grams of unreacted Epon 828: That equated to 15 parts of rubber to 100 total parts of epoxy. This combination had a viscosity of 77,433 cps at 27°C and was still homogeneous after 12 months.

Hypro 1300X18 CTBNX was found to be an acceptable replacement for Hypro 1300X13 CTBN and Hypro1300X31 CTBN (10 wt% bound AN) was also used in place of Hypro 2000X162 CTB. **Table 2** shows a range of adducts that were examined.

Table 2

Example	A	B	C	D
CTB-CTBN or CTB-CTBNX	CTB/CTBN 27% nitrile	CTB/CTBN 27% nitrile	CTB/CTBNX 21% nitrile	CTB/CTBNX 21% nitrile
CTB/CTBN or CTBNX (wt ratio)	1:1	1:2	1:1	1:2
15 PHR Viscosity, 27°C (cps) – initial	77,433	134,800	102,400	223,000
40 PHR Viscosity, 27°C (cps) – initial	436,500	--	697,500	1,192,000
Phase Separation (15 PHR)	none after 1 yr.	none after 6.5 mo.	none after 10 mo.	none after 10 mo.
Phase Separation (40 PHR)	none after 1 yr.	--	none after 10 mo.	none after 10 mo.

The adducts were quite stable at rubber levels of 15 and 40 phr with a DGEBA liquid resin for an extended period of time.

Adhesive Results

The adducts in **Table 2** were formulated into a substituted urea accelerated dicyandiamide cured epoxy paste adhesive. The recipe was a typical one used in RLP/epoxy adhesive studies. Acetone wiped electrogalvanized steel substrates were the adherends. Cure conditions were 30 minutes at 177˚C. **Table 3** contains the T-peel (ASTM D-1876) and lap shear (ASTM D-1002) adhesives data.

Example 1 represents a control noting that HyPox™ RA1340 is an epoxy/1300X13 CTBN adduct. Examples 2-5 are based on the novel adducts prepared with either CTB/CTBN or CTB/CTBNX combinations. The epoxy adhesives contained a rubber level of 15 phr. The weight ratio reflects the concentration of CTB to either CTBN or CTBNX in the adhesive. For instance, example 2 contained 7.5 parts of CTB and 7.5 parts of CTBN 1300X13, example 3 contained 5 parts of CTB and 10 parts of 1300X13 CTBN, etc.

Table 3

Example	1	2	3	4	5
CTB/CTBN or CTB/CTBNX	Hypox RA1340	CTB/CTBN (27% nitrile)	CTB/CTBN (27% nitrile)	CTB/CTBNX (21% nitrile)	CTB/CTBNX (21% nitrile)
CTB/CTBN or CTBNX (wt ratio)	--	1:1	1:2	1:1	1:2
T-Peel (N/mm), RT	9.37 ± .12	5.89 ± 0.14	5.47 ± 0.15	6.5 ± 0.39	7.17 ± 0.27
T-Peel (N/mm), -40°C	2.03 ± 0.17	6.08 ± 0.28	3.4 ± 0.54	7.32 ± 0.19	6.21 ± 0.53
Lap Shear (MPa) 90°C	7.0 ± 0.15	7.1 ± 0.03	6.8 ± 0.03	7.1 ± 0.05	7.3 ± 0.01
T-Peel (N/mm), RT (aged 2.5 months)	9.07 ± 0.32	9.52 ± 0.33	10.1 ± 0.33	8.04 ± 0.20	8.29 ± 0.66
T-Peel (N/mm), -40°C (aged 2.5 months)	2.83 ± 0.51	9.73 ± 0.14	9.07 ± 0.28	9.46 ± 0.39	7.47 ± 0.23
Lap Shear (MPa), 90°C (aged 2.5 months)	7.1 ± 0.02	7.1 ± 0.05	7.3 ± 0.19	7.5 ± 0.05	7.4 ± 0.03
T-Peel (N/mm), RT (aged 6 months)	8.24 ± 0.12	9.42 ± 1.08	9.39 ± 0.59	--	--
T-Peel (N/mm), -40°C (aged 6 months)	2.68 ± 0.31	8.71 ± 0.22	7.25±0.24	--	--
Lap Shear (MPa) (aged 6 months)	7.6 ± 0.10	7.7 ± 0.08	7.7 ± 0.03	--	--

Two notable items in **Table 3** include 1) the low temperature properties are vastly improved using the novel adduct and 2) the low temperature properties are further enhanced after the adhesives are aged for a couple to several months at room temperatures. The mechanism associated with such an increase in T-peel strength is not understood but high peel values are reproducible in both cases of CTB/CTBN and CTB/CTBNX modification.

Preliminary work suggests that these CTB/CTBN-epoxy adducts are not as effective in two component amine cured epoxy adhesives as they are in dicyandiamide cured epoxy adhesives.

Summary

Emerald Performance Materials has developed new, patent pending, technology in RLP epoxy adduct synthesis. These adducts do not separate when diluted with standard DGEBA resins and, when formulated into an adhesive, provide excellent low temperature properties. The new technology combines the good room temperature performance of CTBN with improved low temperature properties.

Generally the rubber modified epoxy resins introduced here can be used in paste and film structural adhesives, for the production of various specific articles, components, and structural forms in numerous applications such as bonding automotive and aerospace components. The toughened epoxy adhesives are desirable in any material or bonding application requiring excellent low temperature toughness as well as impact resistance.

Addendum

Structure for novel RLP-epoxy adduct**:**