IMPROVED LOW TEMPERATURE PERFORMANCE OF EPOXY ADHESIVES

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Introduction

Among thermosetting resins, epoxy resins are widely used in the area of adhesives and sealants, coatings, advanced composites and insulating materials. These resins exhibit good adhesive strength, high strength and hardness and excellent heat and chemical resistance. Because of their high crosslink density, epoxy resins are inherently brittle. A common method of toughening epoxy resins is to incorporate a reactive rubber into the system which separates as a second phase via spinodal decomposition [1] or nucleation and growth [2] upon curing. The second phase increases toughness by three mechanisms. Localized shear yielding, or shear banding and internal cavitation, or interfacial debonding, of the rubbery particles [3] are principal energy dissipating mechanisms with rubber bridging a minor third contributor to toughness.

One of the more common methods of introducing this second phase is to use carboxyl terminated poly(butadiene/acrylonitrile), CTBN, as the reactive liquid polymer. [4,5]. In order to incorporate the rubber in the most efficient manner into the system the CTBN is typically first reacted with an epoxy resin [6] and then dissolved into the bulk of the epoxy. It is important that the rubber adduct be soluble in the main epoxy so that there is no phase separation before curing. In order to achieve rubber miscibility with the epoxy resin, CTBN rubbers are chosen with an acrylonitrile content such that their solubility parameter is close to that of the epoxy. The higher the acrylonitrile level in the CTBN the greater the solubility. The formulator must balance his formulation to achieve good phase separation upon curing and reduce rubber solubility in the resin matrix to minimize modulus and T_g reduction. This approach has provided systems with superior toughness to unmodified epoxies particularly noting high room and elevated temperature adhesive strength [7,8]. Low temperature performance of CTBN elastomer modified epoxy resins, particularly adhesives, is enhanced as well. Yet there are industrial adhesive applications requiring even greater low temperature impact wedge peel strength as those encountered in the automotive market. Epoxy systems with reactive liquid polymers with a lower T_g would give better low temperature performance. Carboxyl terminated polymers, with little or no bound acrylonitrile, have a lower T_g but form adducts that separate into two phases upon aging. This paper will describe the formation of an adduct using reactive liquid polymers with widely separate T_g's which does not separate into two phases upon aging. Previous researchers have combined RLP's of varying T_g for enhanced performance, but did not report any improvement in low temperature performance[9]. One part epoxy adhesives made from these novel adducts show enhanced toughness when tested at elevated, room and low temperatures.

Experimental

The epoxy resin used was a diglycidyl ether of bisphenol A (DGEBA) (Either Epalloy™ 7190 from CVC Thermoset Specialties, an Emerald Performance Materials Company or Epon™ 828 from Hexion™ Specialty Chemicals). Four reactive liquid polymers, available from CVC Thermoset Specialties, were used in this study. Hypro™ CTB 2000x162 is a carboxyl terminated polybutadiene. Hypro™ CTBN 1300X13, CTBN(X) 1300X18 or CTBN 1300X8 are carboxyl terminated poly(butadiene/acrylonitrile) copolymers. Properties are shown in Table 1.

Table 1: Hypro™ CTB and CTBN(X) Properties

RLP Type	**CTB 2000x162**	**CTBN 1300x8**	**CTBNX 1300x18**	**CTBN 1300x13**
Acrylonitrile Content (%)	0	18	21.5	26
Equivalents per hundred resin (Ephr)	0.045	0.052	0.070	0.057
Brookfield Viscosity (cP @ 27°C)	60,000	135,000	350,000	500,000
Solubility Parameter (cal/cm^3)	8.14	8.82	8.99	9.15
Specific Gravity (25°/25°C)	0.907	0.948	0.961	0.960
Functionality	1.9	1.8	2.4	1.8
Molecular Weight (Mn)	4,200	3,550	3,400	3,150
T_g (°C)	-77	-52	-46	-39

The CTBNX, 1300x18, has additional acid functionality which is randomly pendant along the polymer chain. Omicure™ DDA 10 from CVC Thermoset Specialties, an Emerald Performance Materials Company or Amicure® CG-1400 from Air Products and Chemicals, Inc., is used as a dicyandiamide curative, and Omicure™ U-405 from CVC Thermoset Specialties, an Emerald Performance Materials Company or Amicure® UR from Air Products and Chemicals, Inc., is used as a dicyandiamide accelerator. Cab-O-Sil® TS-720 is an amorphous fumed silica obtained from Cabot Corporation and is used as a filler. Substrates are 1" x 4" electrogalvanized steel coupons received from ACT Test Panels, Inc., and were wiped with acetone prior to use.

Synthesis of the epoxy-rubber adduct from CTB and CTBN(X) proceeds as follows. CTB and CTBN(X) are weighed into a three-necked, round bottom flask equipped with mechanical stirring and nitrogen inlet and outlet. The ratio of CTB to CTBN(X) is either 1:1 or 1:2 by weight. Epoxy, typically the diglycidyl ether of bisphenol A, DGEBA, is added to the CTB:CTBN(X) mixture at a carboxyl to epoxy functionality ratio of 1 to 2. The reaction is heated to 120°C under a slow nitrogen purge and reacted to an Ephr endpoint of $\leq$ 0.001, measured by colorimetric titration. Typical reaction times are approximately 10 hours. The reaction temperature is lowered to 100°C and the adduct is further diluted with epoxy to achieve either a 40 phr (parts rubber per hundred resin) or 15 phr solution. The 40 phr and 15 phr solutions were then kept at ambient conditions and observed for phase separation in a 100 ml graduated cylinder. Adhesives were made from the 15 phr solutions according to the following recipe:

100 parts epoxy
15 parts rubber
5.75 parts dicyandiamide curative
2.30 parts urea accelerator
3.45 parts fumed silica

All adhesives were mixed for 15 minutes under high speed, high shear stirring and then degassed for 15 minutes to remove air bubbles. Adhesives were then applied to electrogalvanized steel coupons using 10 mil glass beads as a spacer, and were cured for 30 minutes at 177°C. The uncured adhesives were also aged at ambient conditions for a time period of 2.5 months, after which time they were applied to acetone wiped electrogalvanized steel coupons as previously described and cured. All cured adhesives were tested for T-peel adhesion at room temperature and -40°C by ASTM D-1876 and lap shear adhesion at 90°C by ASTM D-1002. T_g's of the selected cured adhesives were also measured by DSC.

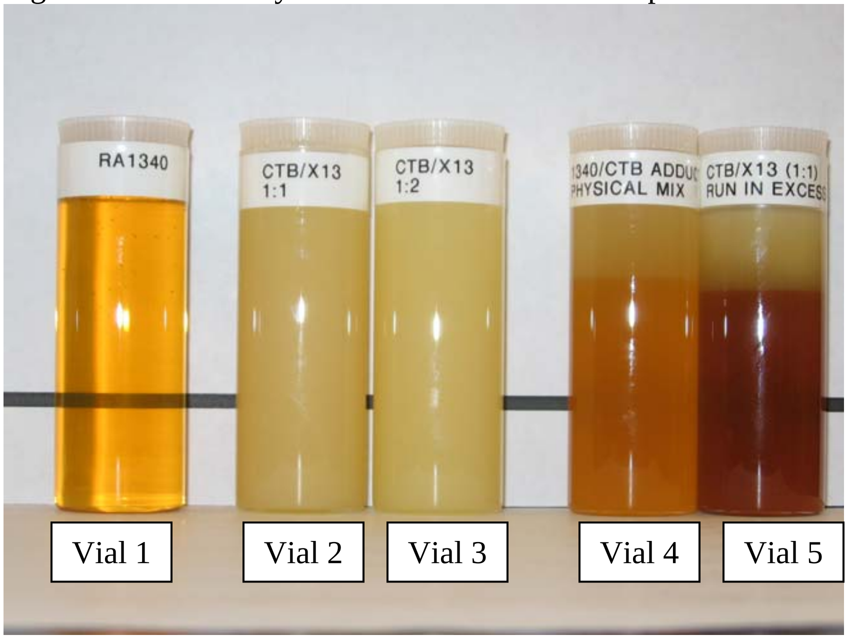
Results and Discussion

The reaction between the CTB, CTBN(X) and epoxy is done at a 1:2 stoichiometric number of carboxyl to epoxy equivalents to ensure that the CTB is coupled to a CTBN(X) via a DGEBA unit. Because CTB is linked to CTBN(X) in such a fashion, it becomes dispersible in neat epoxy and does not phase separate over time. The proposed idealized structure for this adduct is shown in Figure 1.

Figure 1: Proposed Idealized Structure of CTB:CTBN(X) Epoxy Adduct

Figure 2 demonstrates the effect of preparing the adduct at a ratio other than stoichiometric.

Figure 2: Effect of Synthetic Method on Phase Separation



Vial 1 in Figure 2 shows HyPox™ RA1340, which is an adduct of CTBN 1300x13 and DGEBA at a weight ratio of 40 parts of CTBN to 60 parts of epoxy. As would be expected, since the acrylonitrile content of the CTBN is approximately 26% and there is an excess of epoxy during reaction, this adduct is completely miscible in epoxy resin and is extremely clear. The printed black line that can be seen through Vial 1 demonstrates the clarity of this adduct. Vials 2 and 3 shown in Figure 2 represent the CTB (0% acrylonitrile) / 1300x13 (26% acrylonitrile) adduct, at a 1:1 and 1:2 ratio by weight respectively. The adducts are not completely clear, but when spread in thin films are semi-transparent. The adducts will not phase separate at ambient temperatures for extended periods of time (> 1 year) or when exposed to elevated temperatures (80°C). Vials 4 and 5 shown in Figure 2 clearly show phase separation and stress the importance of performing the reaction at a carboxyl to epoxy functionality of 1 to 2. Vial 4 shows a physical mixture of a CTB/epoxy adduct (CTB:DGEBA 4:6 w/w) synthesized separately and then mixed with an equal weight of RA1340. The fact that this mixture readily phase separates demonstrates the need to couple the CTB to a higher acrylonitrile CTBN. Without this coupling and simple epoxy termination of both the CTB and CTBN, the adducted CTB will remain incompatible with the epoxy matrix and will phase separate. Vial 5 represents the one-pot reaction of CTB:1300x13 (1:1), but run in an excess of epoxy, where the rubber portion constitutes 40 percent by weight and the epoxy portion constitutes 60 percent by weight. Because the reaction is run in an excess of epoxy, there is little or no coupling of the CTB to the x13, resulting in separate epoxy end capped CTB and 1300x13, and thus gross phase separation. Thus it can be seen that only when the reaction is run at a carboxyl to epoxy functionality of 1 to 2 will there be sufficient coupling of the CTB to the 1300x13 to ensure compatibility and eliminate phase separation.

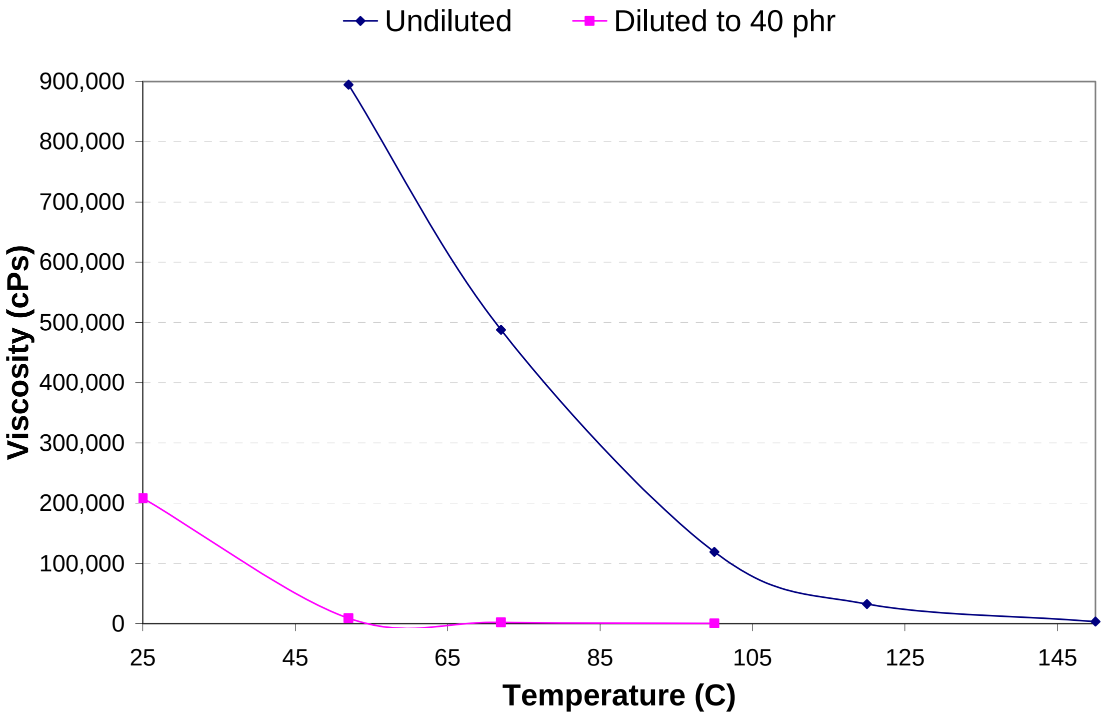
Physical properties and phase separation data for typical reactions are given in Table 2.

Table 2: Physical Properties and Phase Separation of CTB:CTBN(X) Adducts

RLP	**CTB**	**1340 (x13)**	**CTB/x13**	**CTB/x13**	**CTB/x18**	**CTB/x18**	**CTB/x8**	**CTB/x8**
Ratio	**Control**	**Control**	**(1:1)**	**(1:2)**	**(1:1)**	**(1:2)**	**(1:2)**	**(1:1)**
Acrylonitrile Content of RLP	**0%**	**26%**	**26%**	**26%**	**21.5%**	**21.5%**	**18%**	**18%**
15 PHR Viscosity, 27°C (cps)	--	67,567	77,433	71,000	102,400	223,000	67,333	58,067
40 PHR Viscosity, 27°C (cps)	--	198,200	205,000	360,000	697,500	1,192,000	--	--
EEW	--	~ 330	2,077	2,067	1,863	1,736	1,891	1,932
Phase Separation (15 PHR)	--	None after 1 yr.	None after 1 yr.	None after 1 yr.	None after 10 mo.	None after 10 mo.	Sig. sep, 3 layers	Sig. sep. 3 layers
Phase Separation (40 PHR)	Phase sep. after 24 hrs.	None after 1 yr.	None after 1 yr.	None after 1 yr.	None after 10 mo.	None after 10 mo.	--	--

As demonstrated in Table 2, the miscibility of CTB:CTBN(X) adducts at ratios of 1:1 and 1:2 is largely driven by the acrylonitrile content of the CTBN(X) portion of the adduct, with higher acrylonitrile content giving better solubility in epoxy. From this study, an acrylonitrile content of greater than 18% is required for the CTBN(X) portion of the adduct to ensure miscibility. Below an acrylonitrile content of 18%, phase separation is seen at ambient conditions after a period of approximately three months. The epoxy equivalent weight, or EEW, was measured on the CTB:1300x13 adducts before dilution with epoxy. The high EEWs (~2,000) further imply that some coupling of the CTB and 1300x13 has occurred. The CTB/CTBN adducts are further diluted with epoxy due to the fact that the reaction performed at the carboxyl to epoxy functionality of 1 to 2 forms an extremely viscous polymer. The viscosity of the CTB:1300x13 adduct (1:1), when diluted with epoxy to a concentration of 40 phr, gives viscosity approximately equivalent to the RA1340 adduct at an equivalent concentration, with a measured viscosity of approximately 200,000 cPs at 27°C. Figure 3 gives the viscosity profile of the CTB:1300x13 adduct, 1:1, as measured on a cone and plate viscometer, and clearly shows the high viscosity of the undiluted reaction and also shows that when diluted to 40 phr with epoxy, the viscosity is quite negotiable.

Figure 3: Viscosity Profile of CTB/1300x13 Adduct (1:1)



Each of the adducts listed in Table 2 that did not show phase separation was formulated into an adhesive as described in the experimental section, and tested initially and after 2.5 months for T-peel and lap shear adhesion. Results are given in Tables 3 and 4. The CTB adduct was run as a control for low temperature properties and formulated into an adhesive immediately after synthesis of the adduct to ensure that no phase separation had occurred.

The addition of RLP to the adhesive formulation in the form of the RA1340 control shows a significant increase in the T-Peel at room temperature compared to the unmodified adhesive, both in the initial and aged adhesive. However, the T-Peel at low temperature (-40°C) for the RA1340 control only gives a modest improvement compared to the unmodified adhesive. In comparison, the CTB:CTBN(X) adducts show a dramatic improvement in low temperature T-Peel compared to both the RA1340 control and unmodified adhesive, with room temperature T-Peel being comparable to or exceeding the RA1340 control. Upon aging at ambient conditions for 2.5 months, the low temperature performance of the CTB:CTBN(X) continues to improve and in many cases matches or exceeds the room temperature T-Peel of RA1340. The low temperature properties of CTB:CTBN(X) adducts are drastically improved due to the inclusion of CTB, which has a significantly lower T_g than the CTBN(X). The lap shear values were also measured at 90°C, and no significant difference was noted between the CTB:CTBN(X) adducts and the RA1340 control, in either the initial adhesive or the ambient aged adhesives. The T_g of the cured adhesives containing the RA1340 adduct or CTB:CTBN(X) were measured via MDSC. Compared to the unmodified control containing no rubber, the addition of adduct to the formulation slightly depressed the epoxy T_g, where the CTB:CTBN(X) adduct depresses the T_g to a lesser extent as seen in Table 3. This gives an example of how formulation with the rubber can mitigate the extent of T_g depression in the cured epoxy system using CTBN.

Table 3: Adhesive Properties of CTB:1300x13 Adducts

RLP **Ratio**	**None** **--**	**RA1340 (x13)** **Control**	**CTB** **Control**	**CTB/x13** **(1:1)**	**CTB/x13** **(1:2)**
Tg (°C)	132.7	117.8	--	124.2	--
T-Peel (N/mm), RT	1.31 ± 0.06	6.21 ± 0.07	5.06 ± 1.09	5.89 ± 0.14	5.47 ± 0.15
T-Peel (N/mm), -40ºC	1.27 ± 0.12	2.63 ± 0.38	5.17 ± 0.19	6.08 ± 0.28	3.4 ± 0.54
Lap Shear (lbs), 90ºC	976 ± 2	969 ± 19	990 ± 6	1030 ± 4	981 ± 4
T-Peel (N/mm), RT (aged 2.5 months)	1.80 ± 0.25	9.41 ± 1.02	5.23 ± 0.70	9.52 ± 0.33	10.1 ± 0.33
T-Peel (N/mm), -40ºC (aged 2.5 months)	1.41 ± 0.16	2.7 ± 0.12	5.46 ± 0.51	9.73 ± 0.14	9.07 ± 0.28
Lap Shear (lbs), 90ºC (aged 2.5 months)	977 ± 5.14	973 ± 6.36	--	1030 ± 7	1060 ± 28

Table 4: Adhesive Properties of CTB:1300x18 Adducts

RLP	**None**	**HyPox™ RA1340 (x13)**	**CTB**	**CTB/x18**	**CTB/x18**
Ratio	**--**	**Control**	**Control**	**(1:1)**	**(1:2)**
T-Peel (N/mm), RT	1.31 +/- 0.06	6.21 ± 0.07	5.06 ± 1.09	6.5 ± 0.39	7.17 ± 0.27
T-Peel (N/mm), -40ºC	1.27 ± 0.12	2.63 ± 0.38	5.17 ± 0.19	7.32 ± 0.19	6.21 ± 0.53
Lap Shear (lbs), 90ºC	976 ± 2.0	969 ± 19	990 ± 6	1030 ± 7	1060 ± 2
T-Peel (N/mm), RT (aged 2.5 months)	1.80 ± 0.25	9.41 ± 1.02	5.23 ± 0.70	8.04 ± 0.20	8.29 ± 0.66
T-Peel (N/mm), -40ºC (aged 2.5 months)	1.41 ± 0.16	2.7 ± 0.12	5.46 ± 0.51	9.46 ± 0.39	7.47 ± 0.23
Lap Shear (lbs), 90ºC (aged 2.5 months)	977 ± 5.14	973 ± 6.36	--	1090 ± 7	1080 ± 5

Conclusions

The low temperature T-Peel adhesion of dicyandiamide cured epoxy adhesives was dramatically improved (approximately 3x to 4x improvement versus the RA1340 control) through the inclusion of a CTB:CTBN(X) adduct. The excellent room temperature T-Peel and lap shear results are also maintained when the CTB:CTBN(X) adduct is used at a 15 part level. Miscibility of the adduct in the epoxy matrix is also achieved through the incorporation of the CTB:CTBN(X) adduct, with the acrylonitrile content of the CTBN(X) portion of the adduct being critical to the miscibility. Formerly, the incorporation of CTB into an epoxy matrix would cause significant phase separation. Thus this novel synthesis introduces a toughener for thermoset resins that shows both superior room temperature and low temperature adhesive performance while maintaining system compatibility.

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