Better bonding

Optimising the use of reactive liquid polymers to toughen epoxies

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Epoxy adhesives offer excellent properties but are intrinsically brittle due to their high crosslink density. To increase toughness, reactive liquid polymers (RLPs) are often added. Selection of the correct reactive end group is critical. New RLP chemistries are discussed that improve performance at room temperature and in low-temperature applications.

Reactive liquid polymers (RLP) have been used successfully for decades to improve the toughness of adhesives, particularly epoxy adhesives. Manufacturers modify RLPs to introduce alternative reactive end groups, and the selection of RLP end group chemistry is dependent on the type of adhesive used to achieve optimal results.

The use of and results achievable with different types of RLP are reviewed, and new RLP chemistries are discussed that demonstrate exceptional performance for toughening adhesives and also allow more formulation latitude.

Table 1: Typical one-part dicyandiamide epoxy adhesive formulation

Component	Parts
Liquid DGEBA, EEW 187	77.5
ETBN adduct	37.5
Dicyandiamide	8
Urea accelerator	3
Fumed silica	2

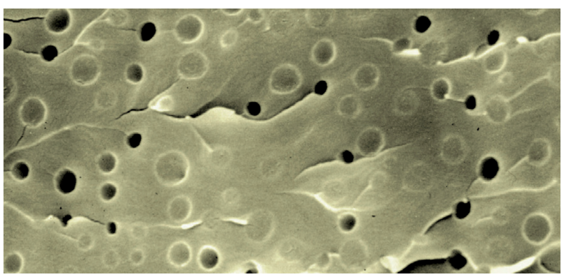

Figure 1: SEM image of cured epoxy using RLP, showing rubbery second phase domains

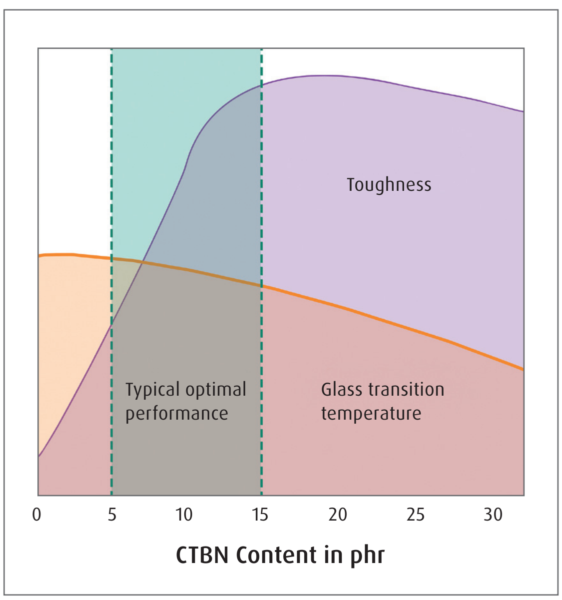

Figure 2: Optimising RLP addition in epoxy adhesives

Why epoxy tougheners are needed and how they work

Among the thermosetting resins, epoxy resins are widely used in adhesives, sealants, coatings, advanced composites and insulating materials. These resins exhibit good adhesive strength, high mechanical strength and hardness and excellent heat and chemical resistance.

However, because of their high crosslink density, epoxy resins are inherently brittle. A common method of toughening them is to incorporate an RLP into the system. The most successfully used RLP is a low molecular weight polybutadiene or polybutadiene-acrylonitrile copolymer with terminal functional reactive groups.

The polymer is initially soluble in the matrix resin, but as the thermoset cures its molecular weight increases and the RLP separates as a second phase via rapid spinodal decomposition [1] or the slower process of nucleation and growth [2]. *Figure 1* shows a typical morphology of a phase separated RLP within a cured epoxy matrix.

The second phase increases toughness via three principal energy-dissipating mechanisms: localised shear yielding, shear banding and internal cavitation or interfacial debonding of the rubbery particles [3], with rubber bridging being a minor contributor to toughness.

Adducting can improve efficiency of RLP tougheners

RLPs are synthesised by a solution free-radical polymerisation, using a carboxylic acid functional azo initiator. This introduces a carboxylic acid group on each end of the low molecular weight polymers, which typically have a molecular weight of 3000-4000.

Direct addition of the carboxyl terminated butadiene acrylonitrile (CTBN) copolymer to an epoxy adhesive typically does not maximise the toughening because the rubber does not react with the epoxy fast enough to provide sufficient phase separation. Therefore, modification of the end group to an epoxy functionality is required to achieve optimum results, and this is most often done through reaction with a diepoxide such as standard diglycidyl ether of bisphenol A (DGEBA) to form a CTBN epoxy adduct [4]

It is important that the CTBN adduct is soluble in the main epoxy so there is no phase separation before curing. To achieve miscibility of the rubber 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 its solubility. The formulator must balance the formulation to achieve good phase separation upon curing and reduce rubber solubility in the resin matrix to minimise reduction in modulus and the glass transition temperature, T_g.
This approach provides superior toughness to unmodified epoxies, particularly in terms of adhesive strength at room and elevated temperatures, with the typical optimum concentration being around 15 phr rubber (parts per 100 parts of epoxy) [5, 6]. The optimisation the formulator must make is represented in *Figure 2*.

Preparation procedure for adducts

A general procedure for preparing a CTBN epoxy adduct is given below. These adducts provide optimal performance in epoxy adhesives compared to direct addition of CTBN rubber.
» Select an epoxy resin compatible with the final product.
» Choose an acrylonitrile level of the CTBN that provides compatibility and performance.
» Combine a weight excess of epoxy to CTBN (typically 60:40 by weight).
» Heat the mixture under nitrogen until the acid number is below 1.
In the reaction, typical temperatures range from 60 °C with catalyst to 110 °C without catalyst. Reaction times vary from 30 minutes to eight hours depending on catalyst and temperature. Typical catalysts used are triphenyl phosphine or other common esterification catalysts.
The epoxy adduct is added to a one-part dicyandiamide structural adhesive to give a rubber concentration of 15 parts per 100 parts of epoxy. The formulation for a one-part epoxy adhesive containing a 40 % by weight CTBN epoxy adduct is given in *Table 1*.
The weight of 37.5 parts of adduct is required to achieve 15 parts of rubber per 100 parts of epoxy (37.5 x 0.40 = 15). The amount of epoxy in the formulation is adjusted accordingly to account for the epoxy introduced into the formulation from the adduct.

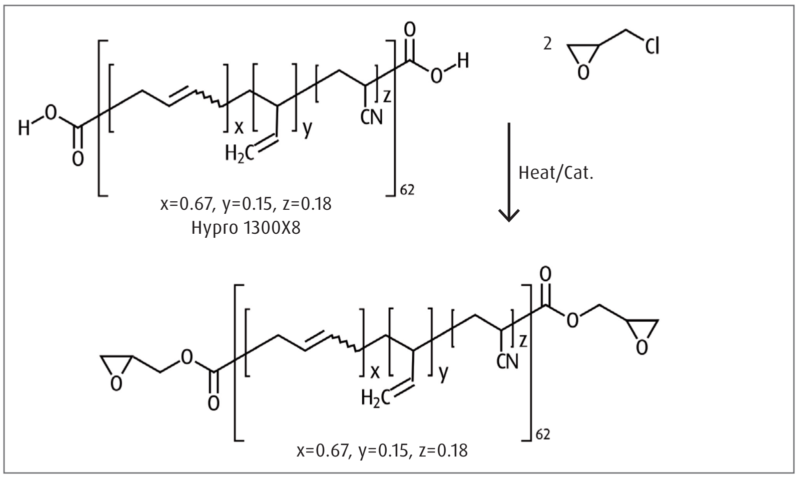

Figure 3: Formation of glycidyl ester from 18 % acrylonitrile CTBN

Advantages offered by direct epoxidation

As indicated above, the use of CTBN epoxy adducts introduces unreacted epoxy into the formulation, which can often be an obstacle when formulating epoxy adhesives. Recent developments in RLP chemistry have now produced an epoxy-terminated butadiene acrylonitrile copolymer (ETBN) directly through the reaction of CTBN with epichlorohydrin to form the glycidyl ester, as shown in *Figure 3*.
In this way, ETBN can be used in an epoxy adhesive without the introduction of unreacted epoxy. The use of glycidyl ester ETBN also offers lower mix viscosity of the epoxy adhesive. For example, a one-part epoxy adhesive as presented in *Table 1* formulated with 15 parts of a traditional 26 % acrylonitrile CTBN epoxy adduct shows a mix viscosity of 130,000 cP at 25 °C, whereas the same formulation using 15 parts of a glycidyl ester ETBN shows a mix viscosity of 61,000 cP at 25 °C.

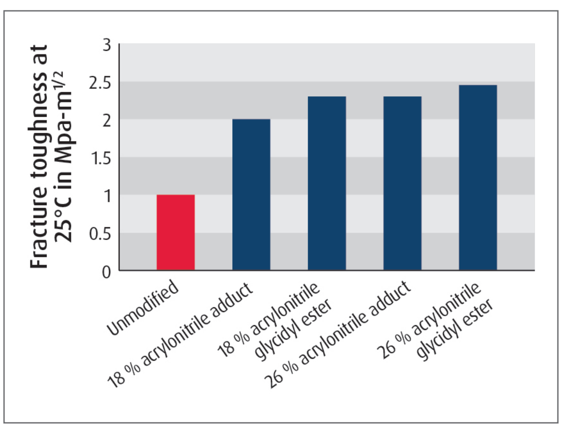

Figure 4: Fracture toughness of one-part epoxies containing 15 phr ETBN

Results at a glance

››› Epoxy adhesives have many excellent properties in high-performance applications but are intrinsically brittle due to their high crosslink density. To increase toughness, reactive liquid polymers (RLPs) are often added.

››› Selection of the correct reactive end group is critical for success: epoxy termination for one-part adhesives and amine or epoxy termination for two-part adhesives. Methacrylate termination can be used in acrylic adhesives or those that are free radical, peroxide or UV cured.

››› New epoxy termination chemistry has created epoxy terminated polymers that are 100 % rubber, offering the formulator more latitude without introducing free epoxy, while also minimising viscosity effects.

››› Other new epoxy adducts solubilise low T_g RLPs and provide exceptional low temperature performance for epoxy adhesives.

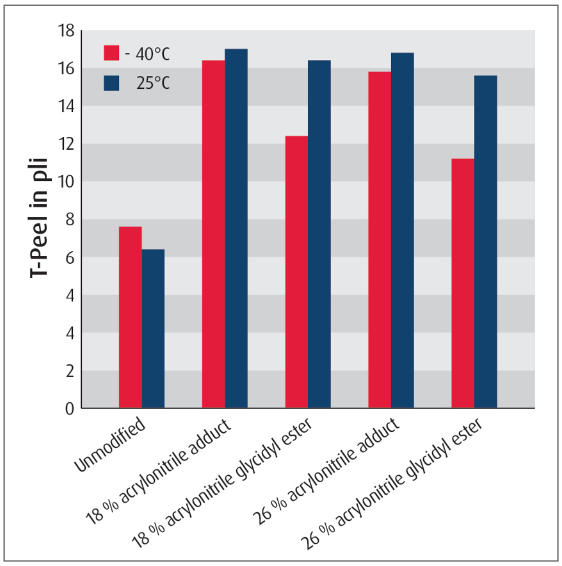

Figure 5: T-peel values on one-part epoxy adhesives containing 15 phr ETBN

Improvements shown in toughness and bond strength

To demonstrate the toughness improvements that are achievable through the incorporation of CTBN epoxy adducts and glycidyl ester ETBN, one-part epoxies were formulated with 15 phr of 18 % acrylonitrile and 26 % acrylonitrile epoxy adducts and glycidyl ester ETBN.

Fracture toughness, which is the ability of a material with a crack to resist fracture, was tested according to ASTM D5045. The results in *Figure 4* show the improvements achievable in fracture toughness through the incorporation of ETBN in epoxies, with a greater than 200 % increase in fracture toughness with 15 phr of the 26 % acrylonitrile glycidyl ester ETBN.

Other commonly used industrial methods of evaluating improvements in epoxy adhesives are T-peel and lap shear tests. The same formulations as above were tested for T-peel adhesion in accordance with ASTM D1876 and lap shear according to ASTM D1002 on phosphate treated, cold rolled steel at different testing temperatures.

The results are shown in *Figures 5* and *6*. Again, the incorporation of 15 phr of either the epoxy adduct or glycidyl ester ETBN shows significant improvement in both T-peel and lap shear performance.

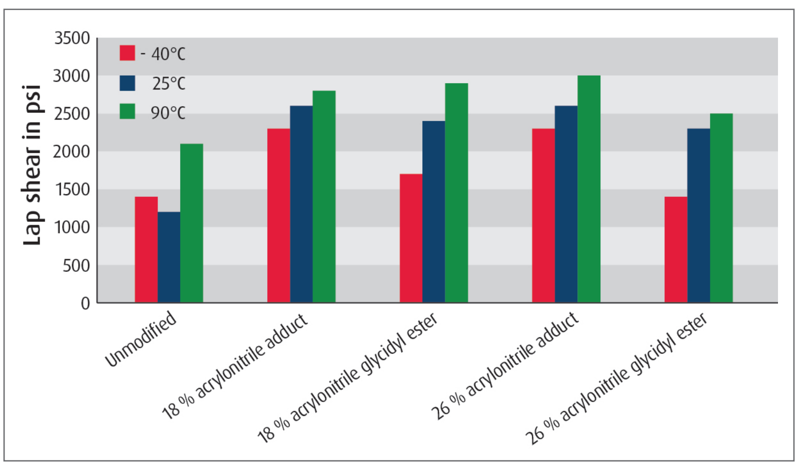

Figure 6: Lap shear test results on one-part epoxy adhesives containing 15 phr ETBN

Improving low temperature performance

Figures 5 and *6* show that the improvements in room temperature T-peel and lap shear are greater at room temperature (25 °C) than at low temperature (- 40 °C). There are industrial adhesive applications, such as automotive and aerospace, that require high performance at -40 °C, which can be facilitated by epoxy systems with a lower T_g RLP.

RLPs with little to no bound acrylonitrile have a lower T_g, but are not miscible with epoxy resins and form adducts that separate into two phases upon storage. US Patent 7,847,026 [7] details a novel synthetic method for producing an adduct that solubilises carboxyl terminated polybutadiene (CTB) with a T_g of - 80 °C for improved low temperature performance.

Carboxyl terminated polybutadiene is combined with a CTBN of 26 % acrylonitrile at a 1:1 ratio by weight with the stoichiometric level of epoxy, and adducted in a procedure similar to that described earlier. This forms a block copolymer of CTB and CTBN connected with DGEBA epoxy and capped with epoxy.

The adduct shows no phase separation after one year storage at ambient temperature. The 25 °C and - 40 °C adhesive strength of the CTB:CTBN adduct shows excellent performance initially after formulation and actually improves after the adhesive is stored for approximately three months at ambient temperature.

This adduct was formulated into a one-part epoxy adhesive at 15 phr and tested for T-peel on electrogalvanised steel after three months at ambient temperature according to ASTM-D1876. The results are presented in *Figure 7*. Incorporating the CTB into the epoxy adduct improves the low-temperature T-peel by more than 300 % on electrogalvanised steel compared to the traditional 26 % acrylonitrile CTBN epoxy adduct. This is a significant advance for toughening in low-temperature adhesives.

Choosing RLPS for two-part epoxy adhesives

The use of epoxy terminated RLP in one-part epoxy adhesives has been considered above. In two-part amine cured epoxy adhesives, RLPS can be found either with the amine hardener or with the epoxy portion of the formulation. Again, the proper selection of the reactive end group chemistry is critical to toughening.

If the RLP is to be added to the amine side of the adhesive, then an amine-terminated butadiene acrylonitrile (ATBN) copolymer provides optimum toughening. If the RLP is to be added to the epoxy side of the formulation, then an epoxy-terminated version (ETBN) provides optimum toughening.

The use of RLP on either the amine hardener side or the epoxy resin side will depend on several factors, including compatibility with the chosen amines, viscosity limitations and ultimate toughness of the adhesive. An ATBN should be selected for compatibility with the amine hardener; and generally, ATBNs are not compatible with aliphatic amines.

If ATBNs are incompatible with the chosen amine hardener, then an epoxy adduct or glycidyl ester ETBN should be used on the resin side of the formulation. The addition of RLP to either side will increase viscosity. RLP can therefore be used on whichever side of the formulation allows more latitude for viscosity increase.

The use of ATBN or epoxy adducts does not always give equivalent toughening results when added at similar concentrations. The phase separation kinetics are important to provide optimum morphology for toughening.

Differences in additive efficiency confirmed

A standard DGEBA epoxy resin was cured with a combination of a modified aliphatic amine adduct and polyamide, with the inclusion of 25 phr of either an ATBN containing 18 % acrylonitrile or epoxy adduct containing 18 % or 26 % acrylonitrile. [8] A second system was also evaluated, in which a standard DGEBA epoxy resin was cured only with an aliphatic amine hardener with 15 phr of the same rubbers evaluated in the first system.

The T-peel results evaluated on cold rolled steel in *Figure 8* show that the incorporation of ATBN or epoxy adduct in the system cured with the combination of modified aliphatic amine adduct and polyamide shows excellent results, but for the system cured with the aliphatic amine alone the ATBN does not show any toughening.

This is because, as stated above, ATBN is incompatible with aliphatic amines, and the slow-reacting ATBN in this system does not have a chance to phase separate and provide the proper second phase morphology for toughening. The data also demonstrate that the choice of acrylonitrile level in the epoxy adduct is dependent on the hardener system, and various levels should be tested to ensure optimal results are achieved.

RLPS can be designed for free radical cured adhesives

The use of RLPs to toughen adhesives also extends to other types of systems, such as acrylic, free radical cured or UV cured. It remains true that the proper selection of reactive end group chemistry is critical for achieving optimal results in these types of systems.

Methacrylate (vinyl) terminated RLPs react efficiently into these types of adhesives and generate the proper morphology for toughening. The use level of methacrylate terminated RLP is similar to that in epoxy adhesives, generally 15 phr. In addition to terminal functionality, methacrylate terminated RLP containing acrylonitrile also contains pendant reactive methacrylate groups along the backbone of the polymer chain. This further allows for efficient incorporation of methacrylate terminated RLP into these types of adhesives.

Careful additive selection maximises performance

The use of RLP in epoxy adhesives significantly improves adhesive toughness, whether measured by fracture toughness, T-peel or lap shear testing. The proper RLP selection is critical to optimising performance in the application. The correct reactive end group chemistry and acrylonitrile content should be considered to achieve maximum toughness.

For one-part epoxies, ETBN, whether in the form of an epoxy adduct or glycidyl ester, should be used. Newly-developed, unique epoxy adducts for low temperature performance provide exceptional results at - 40 °C.

For two-part epoxies, ATBN or ETBN can be used, and further consideration must be given to compatibility with the formulation components to avoid phase separation. Thus, the formulator has a variety of options to achieve goals for improving the toughness of the adhesive.

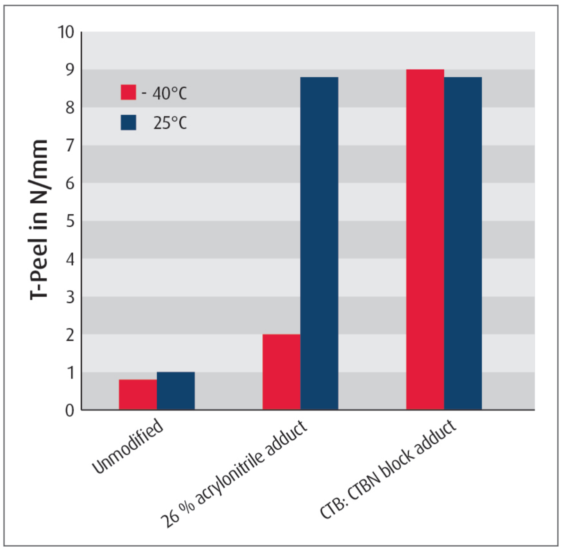

Figure 7: T-peel test results on one-part epoxy adhesive containing 15 phr CTB:CTBN adduct

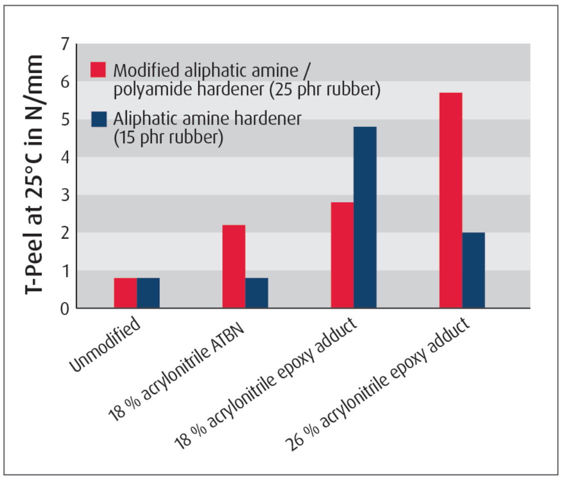

Figure 8: Toughening of two-part, amine cured epoxy adhesives with ATBN or epoxy adduct

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