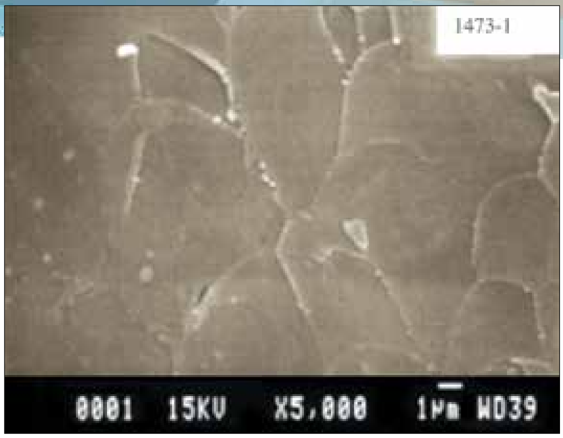
▸Hypro™ Reactive Liquid Polymers (RLP)

Hypro Reactive Liquid Polymers (RLP) are synthetic rubber with chemical functionality. They incorporate rubber properties into brittle thermoset resins, adhesives, coatings and composites.

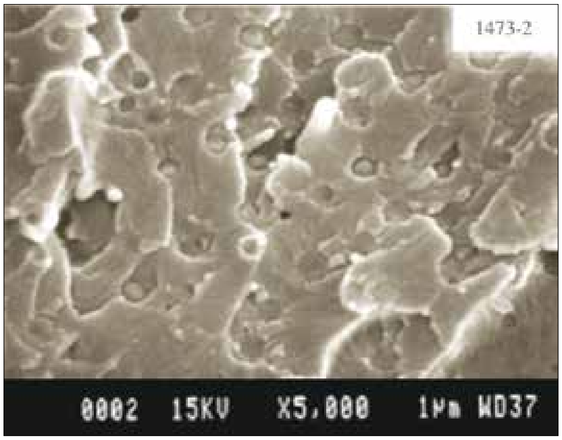
Hypro RLP combine the benefits of a low molecular weight butadiene-acrylonitrile rubber with terminal chemical functionality. They impart toughness, improve adhesion, and extend performance to low temperatures. The toughness shows in many attributes: crack resistance, fracture toughness, impact resistance, resilience, interlaminar adhesion, peel adhesion and thermal cycling.

▸The Hypro RLP Toughening Mechanism

With the proper selection of acrylonitrile content, RLP will be soluble with thermoset resins. When the resin system cures, the Hypro RLP terminal functionality reacts into the thermoset resin, and the synthetic rubber precipitates to form discreet rubber particles. These micron-scale particles absorb strain energy. **Picture 1** shows a magnification of cured epoxy resin. It is a brittle, glassy resin. **Picture 2** shows the same epoxy modified with Hypro RLP. The discrete rubber particles provide the toughening and the epoxy matrix maintains the strength of the unmodified epoxy.



Picture 1. *Cured, Unmodified Epoxy Resin*



Picture 2. *Hypro RLP-Modified Epoxy Resin*

▸Typical Levels – Hypro RLP Toughened Systems

The optimum Hypro RLP level varies with the type of resin. The general guidelines are that most systems require 5 phr to provide enough rubber particles for significant toughening and that above 20 phr enough RLP remains soluble with the resin, and it acts as a flexibilizer in addition to a toughening agent.

Epoxy composites and structural adhesives typically have < 15 phr, and sealants and coatings typically have >25 phr. Unsaturated polyester composites tend to have < 3 phr, and vinyl ester tends to have 5-to-10 phr. Acrylic adhesives and sealants tend to have multiple toughening agents and the Hypro RLP may be up to 20 phr.

Figure 1 graphically depicts the general guideline for RLP incorporation, demonstrating the relationships between CTBN content, T_g and toughness.

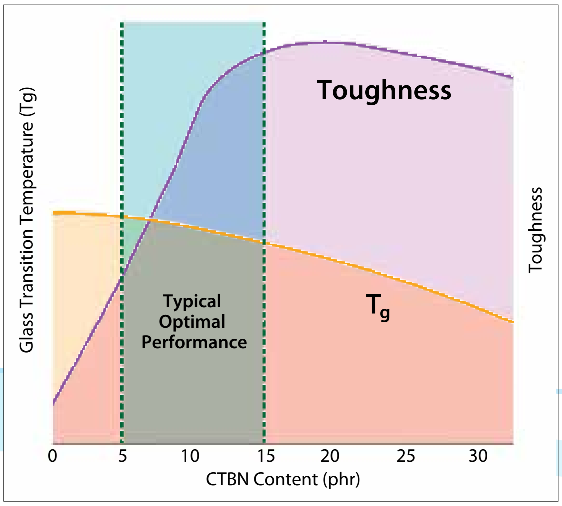


Figure 1. *General Guideline for Hypro RLP incorporation*

Reference bibliography #12, 19 and 23

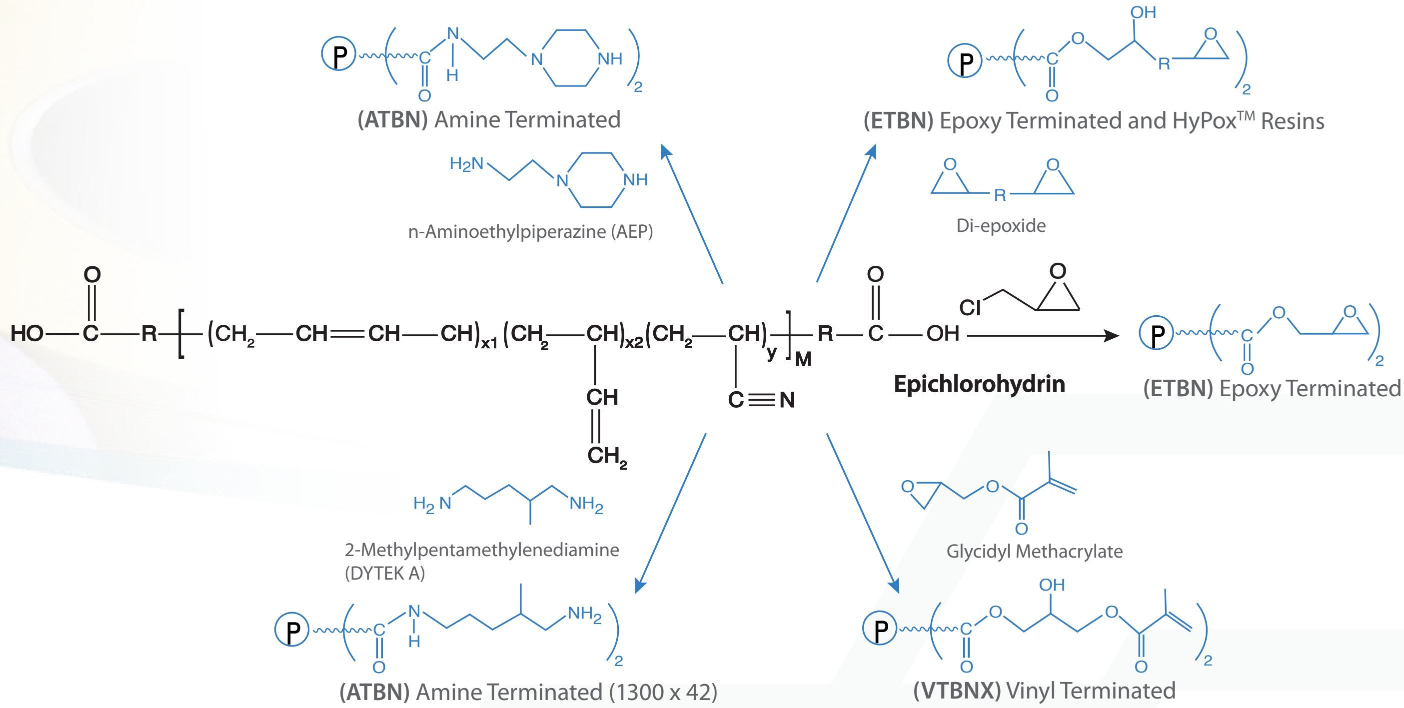


Figure 2. *Hypro CTBN and Derivitives Chemical Structure*

▸Hypro™ Reactive Liquid Polymers (cont.)

Hypro CTBN typically requires chemical modification for effective incorporation into thermoset chemistries. Choice of terminal chemistry will depend on the application and end-use.

CVC Thermoset Specialties offers CTBN with alternative terminal reactivity (**Figure 2**) and the HyPox elastomer-modified epoxy resins for easy incorporation by formulators.

The Hypro CTBN can be used directly in epoxy-anhydride systems and in unsaturated polyester. Other thermoset systems require chemical modification.

Amine Terminated Butadiene-Acrylonitrile (ATBN) are typically used as co-curatives to epoxies and isocyanates in ambient-cure adhesives, coatings, sealants and in some heat-cured composites.

Methacrylate (Vinyl) Terminated Butadiene-Acrylonitrile (VTBNX) can be the primary toughening agent in acrylic adhesives, sealants, and composites and as complementary toughening agents in vinylester and in unsaturated polyester composites and adhesives.

Epoxy-Terminated Butadiene-Acrylonitrile (ETBN) include both glycidyl esters of a CTBN and epoxy adducts of CTBN. Some of these are sold as HyPox Elastomer-Modified Epoxy Resins. The Hypro ETBN and the HyPox resins are toughening agents for epoxy coatings, adhesives and composites. Other specialty applications are as toughening agents for cyanate esters and for unsaturated polyester. Many formulators perform custom reactions with the Hypro CTBN to meet the requirements of their systems.

Hydroxyl-Terminated Butadiene (HTB) is principally used for polyurethane potting compounds, coatings, sealants and other thermosets, providing excellent moisture resistance, electrical insulation, low glass transition temperature and extraordinary compatibility with fillers (**Figure 3**).

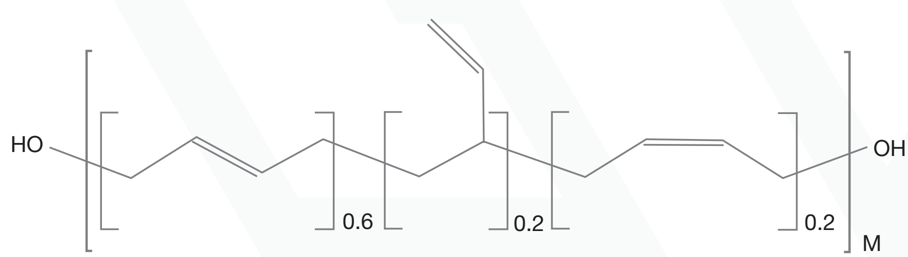


Figure 3. *Hypro HTB Chemical Structure*

▸Guidelines for Pre-Reacting Hypro™ RLP Adducts

The Hypro CTBN synthetic rubbers are butadiene polymers and butadiene-acrylonitrile copolymers with carboxyl groups at the polymer chain ends. Most formulators use a pre-reacted CTBN to attain the optimum benefits. The pre-reaction may be a simple modification of the carboxyl to another reactive moiety or a reaction with resins (typically epoxy or vinyl ester) to make a master batch ready for dilution.

The typical process steps

1. Choose the epoxy resin most compatible with the final product.
2. Choose the Hypro CTBN for the desired compatibility and performance.
3. Combine a molar excess (10:1) or weight excess (60:40) of epoxy to CTBN
4. Heat and react under dry nitrogen with agitation until the acid number is <1.
    a. Typical temperatures range from 60°C with catalyst to 175°C for solid resins
    b. Typical time is 30 minutes-to-7 hours and varies with temperature and catalyst
5. Dilute with additional epoxy resin to the desired CTBN concentration, typically 6-to-12phr for composites and structural adhesives.

Processing options

- Catalysts increase the reaction rate, and the resultant adduct tends to increase in viscosity with time. Catalyst options include triphenyl phosphine (preferred), ethyltriphenylphosphoniumiodide, benzyl dimethyl amine, and other esterification catalysts.
- Epoxy resin can be co-reacted with CTBN to form an adduct. Addition of these adducts in the epoxy matrix increases ductility and toughness after cure.

Other processing notes

- Solid epoxy-CTBN adducts can be made by adducting solid epoxy resin or by advancing liquid epoxy and CTBN with BPA or by vulcanizing CTBN-epoxy adducts.
- Vinyl ester-CTBN adducts can be one step—combine epoxy resin, CTBN, and methacrylic acid and react or multi-step—react epoxy and CTBN before adding and reacting methacrylic acid. This typically requires a stabilizer.
- Water-dispersed CTBN-epoxy adducts for electrodeposition coating require several subsequent steps after producing the CTBN-epoxy adduct.