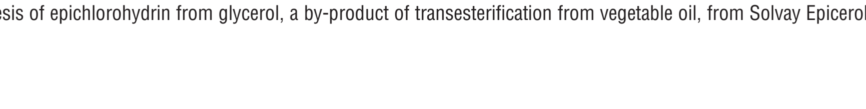
5.02.3.2.2 Epoxy resins

Epoxy resins are an important class of step-growth polymer which has allowed for a quick step technique to synthesize thermoset networks. Epoxy thermosets are reactions between an epoxy resin, a small molecule or prepolymer that is functionalized with epoxide end groups, and a hardener or crosslinking agent. The crosslinking agent has a functionality $f > 2$ to allow for oligomer formation, branching, and finally crosslinking.

One of the interesting factors about epoxy curing arises from the unique geometric structure of the epoxy ring. The development of epichlorohydrin facilitated the wide utility and application of this curing process to extend beyond small-molecule diepoxies and include epoxy-functionalized prepolymers. With the need to be more ecologically mindful, Scheme 8 highlights a green chemistry approach to synthesize epichlorohydrin from glycerol, a transesterification by-product from vegetable oil.

The epoxy ring itself is a heterocyclic three-membered planar ring.[114] Although the chemical compositions of the carbon and oxygen within the ring are sp^3-hybridized and should have characteristic 109.5° tetrahedral structures, the formation of the three-membered ring compresses the internal angles of the epoxy ring to nearly 60°. Thus, the hybridized orbitals of the carbon atoms are more similar to the trigonal planar sp^2 orbitals. Many previous literatures reviewed the effect of chemistry and hyperconjugation of the strained three-membered ring.[115,116] The compressed internal angle of the epoxide ring translates to a very large ring strain energy of approximately 113 kJ mol^{-1}. The release of ring strain contributes to the major driving force for the fast and efficient mode of curing used in thermosets.

The epoxy curing occurs through a complex process in which the dynamics and the polymer structure change during the curing chemistry. The reaction occurring between an epoxy resin and a hardener such as a diamine first occurs through the production of the small oligomers. Because the hardener has a functionality greater than 2, branching and eventual crosslinking will occur. During the branching stage, the polymer is still soluble in the reaction medium; however, as the reaction continues to cure, the reaction product will lose solubility or begin to swell in the reaction solvent and gelation takes place. Because the curing process is such a dynamic and complicated progression, properties of the polymers also change throughout the reaction.[117] In fact, the curing process directly influences the viscoelastic properties as the monomers and reactants transition from oligomers to branched and finally crosslinked networks. The choice of epoxy resin, hardener,



Scheme 8 Synthesis of epichlorohydrin from glycerol, a by-product of transesterification from vegetable oil, from Solvay Epicerol™ process.

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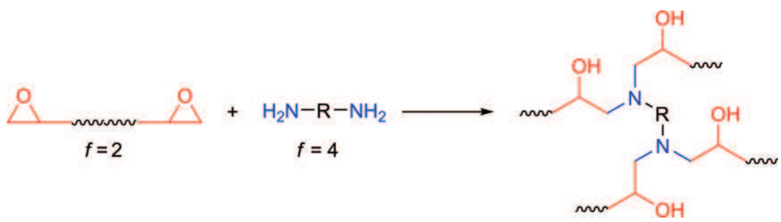

Scheme 9 General epoxy resin curing between a diepoxide (functionality (f) = 2) and diamine (f = 4).

and crosslink density directly influences the polymer storage modulus increase as the epoxy resin cures. Because the chain mobility of the polymer thermoset decreases with crosslinking, the T_g also begins to rise as the curing process occurs.

Scheme 9 represents a general epoxy resin curing reaction between a diepoxide and diamines. The reaction of the epoxide ring can occur between an electrophile or a nucleophile to generate the ring-opening reaction and the subsequent alcohol. In general, the primary and secondary alcohols can be produced, since in theory, both carbons of the epoxide ring are likely to react with the nucleophile or electrophile. However, the sterics of the reaction generally leads to the attack of the less sterically hindered carbon and subsequently the secondary alcohol as seen in Scheme 9. Common nucleophiles used in epoxy reactions are alcohols, amines, and carboxylic acids. Alkyl halides and isocyanates are possible electrophilic reactants with epoxides as well.

Epoxy curing has found vast utility in self-healing applications since the reaction occurs quickly and without any aid of catalysts. In many self-healing systems, microcapsules containing a reactant or catalyst are generated and blended into a binary polymer matrix. Upon stress or mechanical damage, the microcapsule will rupture and react with the surrounding matrix to repair the polymer damage. The curing agent or compound held within the microcapsule contains the same chemistry as the polymer matrix to repair the damage with the same polymer composition to maintain matrix homogeneity. Epoxide reactions offer advantages such as a fast cure which is often necessary for quick polymer repair.

Recently, Sottos and co-workers developed a method to prepare microcapsules containing reactive amines using interfacial polymerization rather than conventional emulsion techniques to create the walls of the microparticles.[118] These particles were intended for epoxy adhesive applications with potential self-healing properties. The capsules contained the very reactive diethylene triamine which was created using a water-in-oil emulsion method and stabilized in a nanoclay suspension with polyisobutylene (PIB). Upon removal of PIB, the particles were quickly reacted with TDI to create a polyurea wall. Careful addition of the TDI allowed for unaggregated microparticles with diameters averaging about $26 \pm 10\,\mu m$ (Figure 21). The amine-containing capsules were blended with epoxy resin and curing was performed upon added pressure to rupture the capsules.

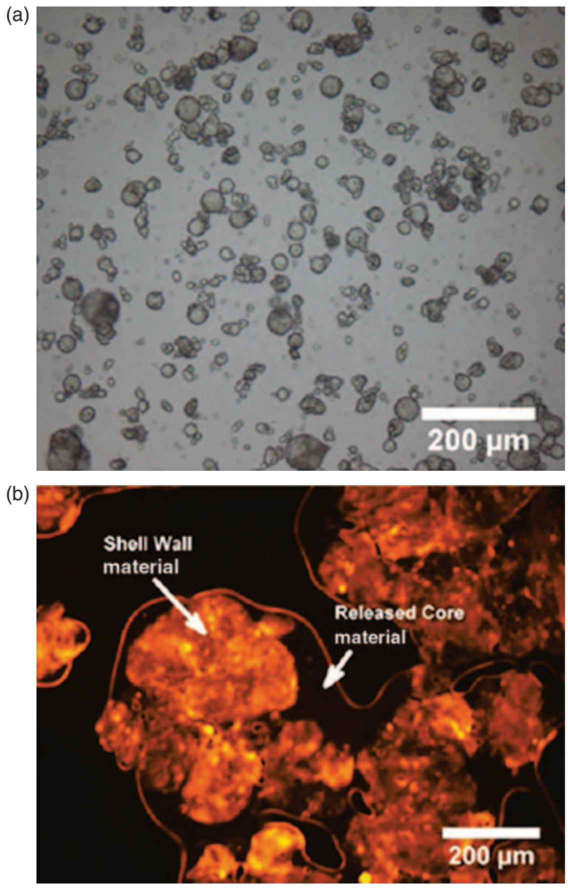

Figure 21 Micrographs of epoxy-cured polymer composites: (a) optical micrograph of amine-filled microcapsules in solution for self-healing epoxy composites; (b) fluorescence micrograph reflecting the response of microcapsules under applied pressure.[118] Reprinted with permission from Wang, W.; Jin, Y.; Ping, P.; *et al. Macromolecules* **2010**, *43* (6), 2942–2947.[111] Copyright (2010) American Chemical Society.