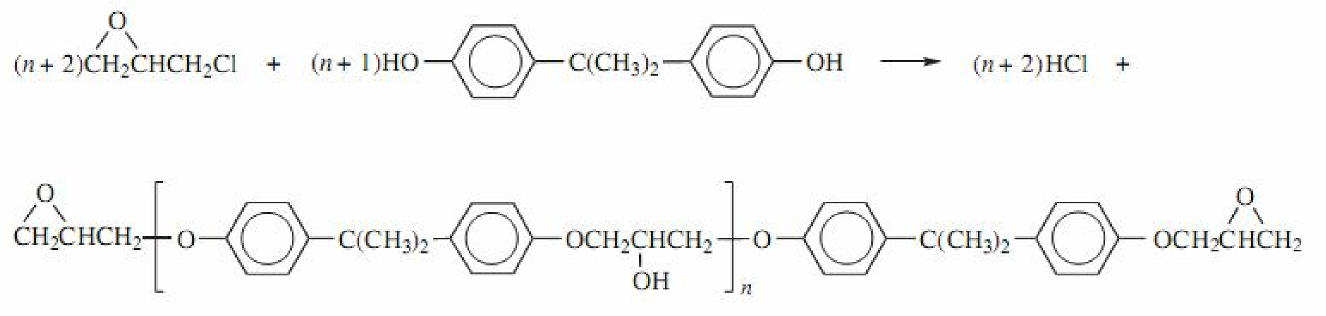
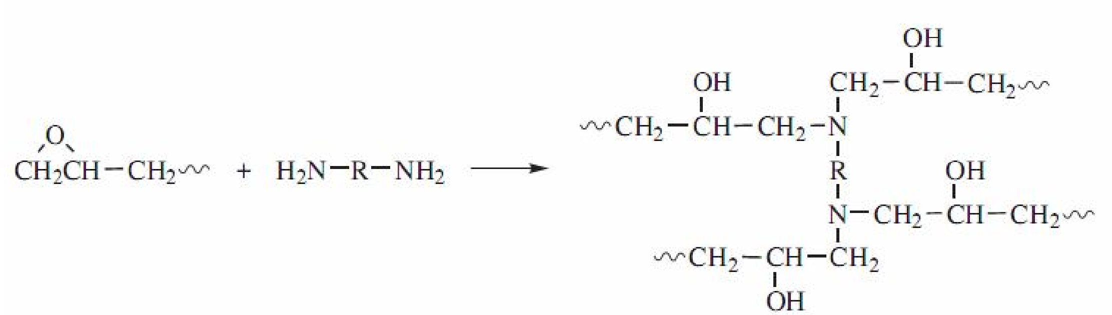
Epoxy resins

Synthesis: Epoxy resins or plastics are typically formed by the reaction of epichlorohydrin and bisphenol A:



The reaction actually involves the sodium salt of bisphenol A since polymerization is carried out in the presence of an equivalent of sodium hydroxide. Reaction temperatures are in the range 50–95 C. Side reactions (hydrolysis of epichlorohydrin, reaction of epichlorohydrin with hydroxyl groups of polymer or impurities) as well as the stoichiometric ratio need to be controlled to produce a prepolymer with two epoxide end groups. Either liquid or solid prepolymers are produced by control of molecular weight; typical values of n are less than 1 for liquid prepolymers and in the range 2-30 for solid prepolymers.

A variety of coreactants are used to cure epoxy resins, either through the epoxide or hydroxyl groups. Polyamines are the most common curing agent with reaction involving ring-opening addition of amine:



Both primary and secondary amines are used; primary amines are more reactive than secondary amines. Since each nitrogen-hydrogen bond is reactive in the curing reaction, primary and secondary amine groups are biand monofunctional, respectively. A variety of amines are used as crosslinking agents, including diethylene triamine, triethylene tetramine, 4,4-diamino-diphenylmethane, and polyaminoamides (e.g., the diamide formed from diethylene triamine and a dimerized or trimerized fatty acid). Other types of compounds have also been used to cure epoxy resins via the epoxide groups, including polythiols, dicyandiamide (cyanoguanidine), diisocyanates, and phenolic prepolymers. Some of these agents require weak bases such as tertiary amines and imidazole derivatives to accelerate the curing process.

Properties: Epoxy resins possess high chemical and corrosion resistance, toughness and flexibility, good mechanical and electrical behavior, and outstanding adhesion to many different substrates. A wide range of products varying in properties and curing temperature are obtained for specific applications by proper selection of the monomers, additives, and curing agents. Use temperatures are in the range 90-130°C.

Applications: The applications for epoxies fall into two categories—coatings and structural. Coatings applications include marine, maintenance, drum, and can coatings. Automotive primer coatings involve epoxy resins with ionic charges (either carboxylate or quaternary ammonium ion) that allow for electrodeposition of the resin. Waterborne epoxy coatings have been developed for beer and beverage containers. Structural composites are used in the military (missile casings, tanks), aircraft (rudders, wing skins, flaps), automobiles (leaf springs, drive shafts), and pipe in the oil, gas, chemical, and mining industries. Laminates are used in the electrical and electronics industries (circuit-board substrate, encapsulation of devices such as transistors, semiconductors, coils). Other applications include industrial and terrazzo flooring, repair of highway concrete cracks, coatings for roads and bridges, and a wide range of adhesive applications.

Polyurethanes

Synthesis: The synthesis of polyurethanes is usually presented as proceeding via the formation of carbamate (urethane) linkages by the reaction of isocyanates and alcohols:

$$n\mathrm{HO{-}R{-}OH} \;+\; n\mathrm{OCN{-}R'{-}NCO} \;\longrightarrow$$

$$\mathrm{HO}\left(\mathrm{R{-}OCONH{-}R'{-}NHCO{-}O}\right)_{(n-1)}\mathrm{R{-}OCONH{-}R'{-}NCO}$$

However, this is an oversimplification since other reactions are also usually involved. Foamed products such as seat cushions and bedding are the largest applications of polyurethanes. Water is often deliberately added in the production of flexible polyurethane foams. Isocyanate groups react with water to form urea linkages in the polymer chain with the evolution of carbon dioxide:

$$2\sim\mathrm{NCO} \;+\; \mathrm{H_2O} \;\longrightarrow\; \sim\mathrm{NH{-}CO{-}NH}\sim \;+\; \mathrm{CO_2}$$

The carbon dioxide acts as the blowing agent to form the foamed structure of the final product. (Low-boiling solvents such as fluorotrichloromethane are usually added to act as blowing agents in the synthesis of rigid polyurethane foamed products.) Many polyurethanes are synthesized using mixtures of diols and diamines. The diamines react with isocyanate groups to introduce additional urea linkages into the polymer. Thus, the typical polyurethane actually contains both urethane and urea repeat units:

$$2\sim NCO + H_2N-R''-NH_2 \longrightarrow \sim NH-CO-NH-R''-NH-CO-NH\sim$$

Properties: The wide variations possible in synthesis give rise to a wide range of polyurethane products including flexible and rigid foams and solid elastomers, extrusions, coatings, and adhesives. Polyurethanes possess good abrasion, tear, and impact resistance coupled with oil and grease resistance.

Applications: Flexible foamed products include upholstered furniture and auto parts (cushions, backs, and arms), mattresses, and carpet underlay. Rigid foamed products with a closed-cell morphology possess excellent insulating properties and find extensive use in commercial roofing, residential sheathing, and insulation for water heaters, tanks, pipes, refrigerators, and freezers. Solid elastomeric products include forklift tires, skateboard wheels, automobile parts (bumpers, fascia, fenders, door panels, gaskets for trunk, windows, windshield, steering wheel, instrument panel), and sporting goods (golf balls, ski boots, football cleats). Many of these foam and solid products are made by reaction injection molding (RIM), a process in which a mixture of the monomers is injected into a mold cavity where polymerization and crosslinking take place to form the product. Reaction injection molding of polyurethanes, involving low-viscosity reaction mixtures and moderate reaction temperatures, is well suited for the economical molding of large objects such as automobile fenders.