Brief Overview of Epoxy Resin Synthesis and Crosslinking

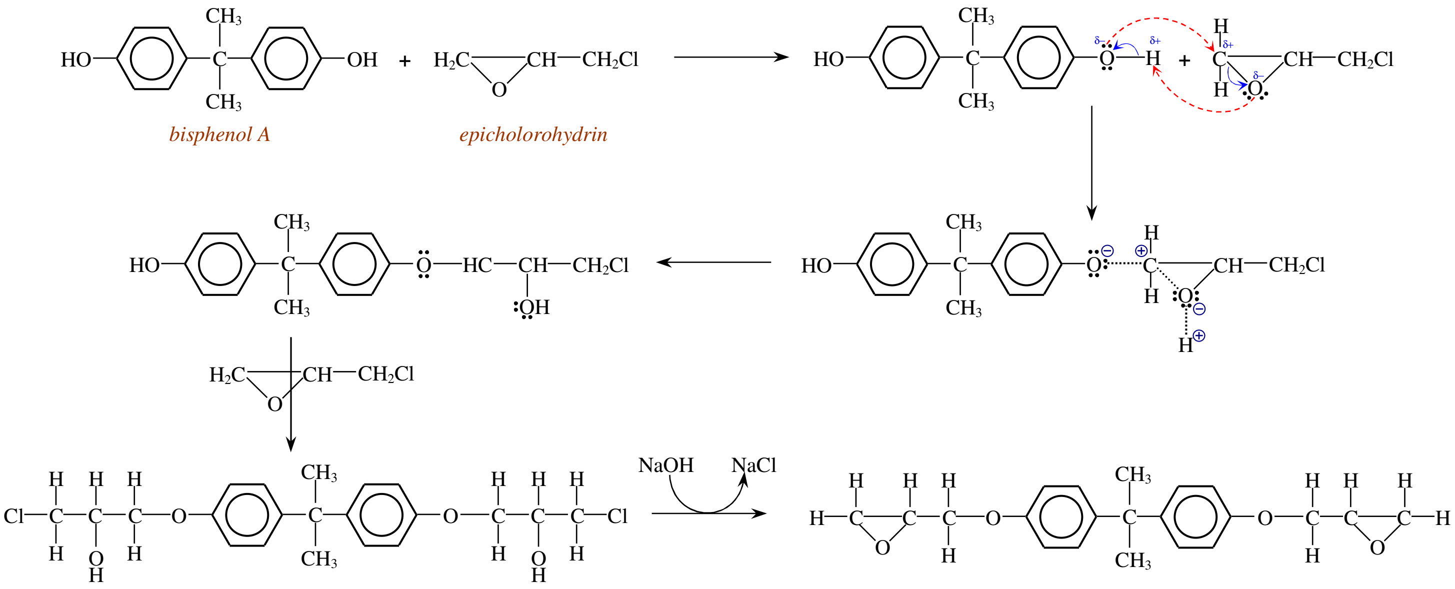
Marshall Space Flight Center Jacobs ESTS Group,

Randy Lee October 2009

Crosslinking of the epoxy chains with amine groups (the primary assignment) will be covered in Section III, but first, let us explore some of the possible reactions and mechanisms associated with the synthesis phase of the epoxy prepolymer.

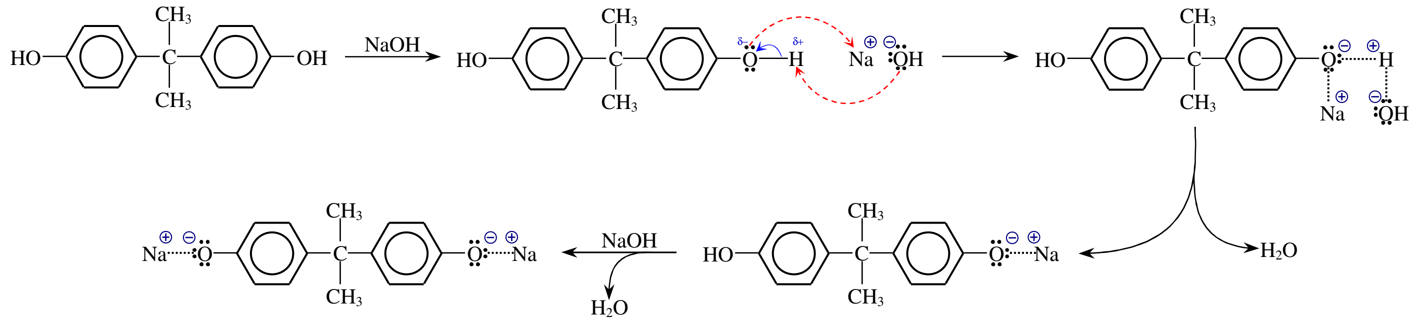
Section I: Prepolymer Synthesis

The scenario given in the book (and reflected in the class lectures) proposes that the prepolymer (Stage A resin) is formed by the ring-opening reaction between the epoxide group and a phenol hydroxyl group which converts the epoxide oxygen to an alcohol and forms a link between the epoxide carbon and the phenoxy group . . . and then in a final washing step, NaOH is used to extract the chloride groups and re-form the epoxide ring. In a 2-to-1 mixture of the chlorohydrin and diphenol, the mechanism and associated reaction sequence might be illustrated by . . .



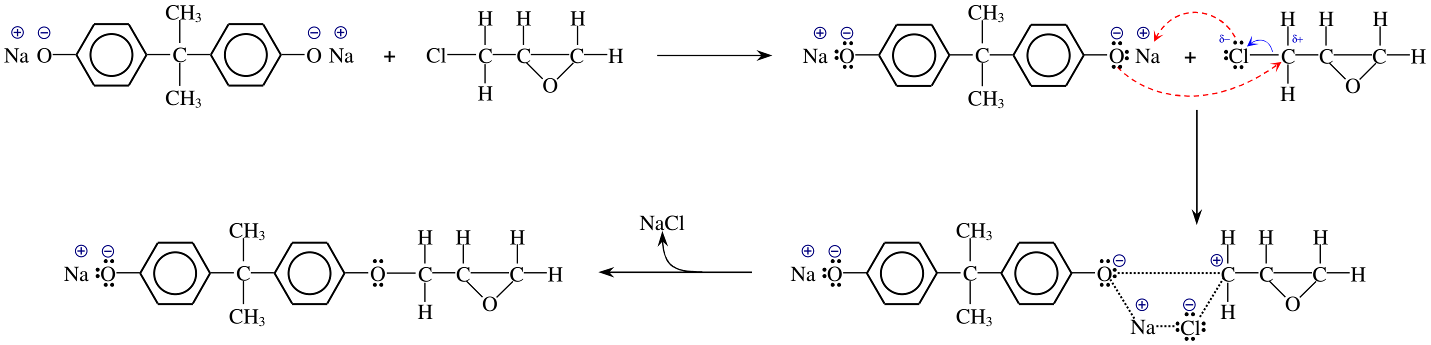
I

Without a doubt, this reaction scheme has its place somewhere in the field of epoxy organic chemistry but how much relevance does it actually have in the real world production and vast industry of epoxy resins used for adhesives and composite matrices? Consider the following scenario which does not involve cleavage of the epoxide ring (at least initially) but rather makes use of the reducing power of the chloride atom on the chlorohydrin (this atom must be attached to the epoxide molecule for some reason, right?). In this approach, NaOH is allowed to react directly with the diol (twice) to form the associated di-salt – before the epoxide is even introduced (locally) into the system . . .



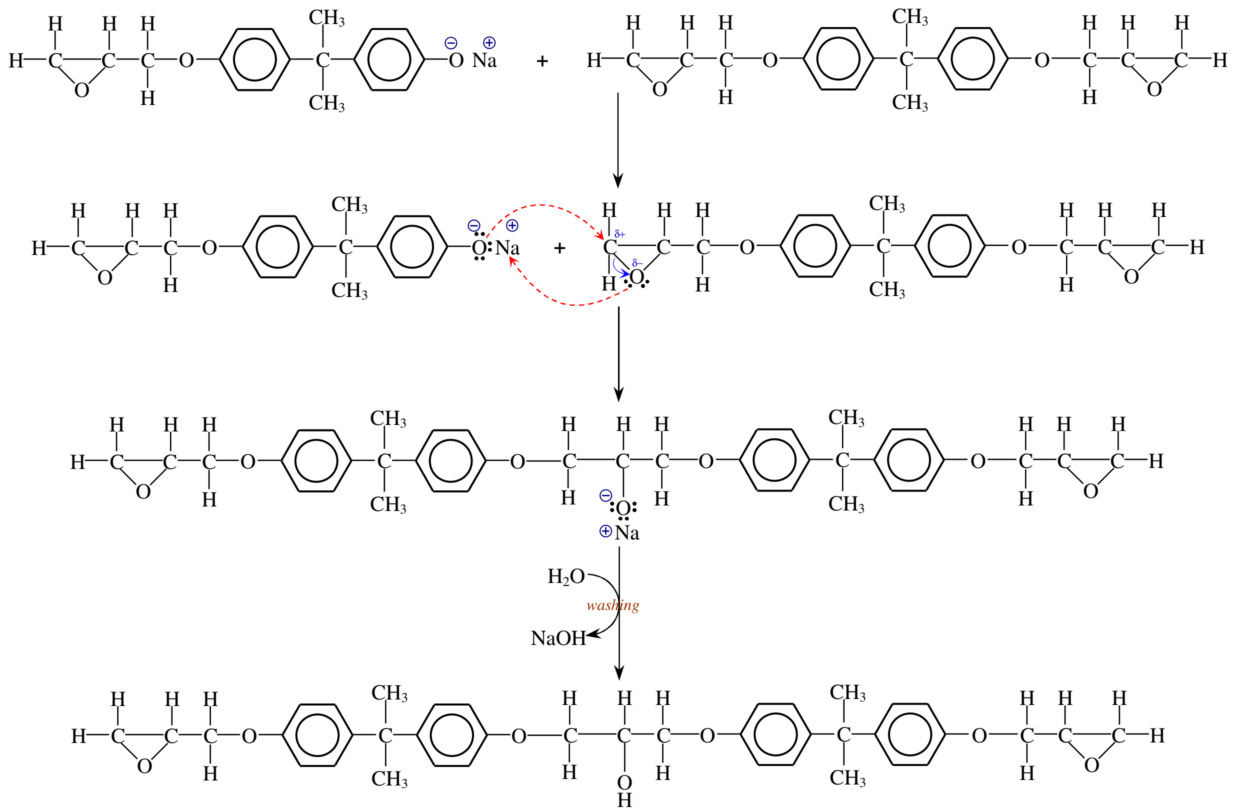
di-sodium salt of bisphenol A

Now . . . when the salt is allowed to react with an incoming chlorohydrin molecule, the nucleophillic phenolate ion attacks the electropositive carbon atom attached directly to the chloride atom . . .



If two parts of epichlorohydrin were used in this system, the second one would combine with the sodium phenoxy group on the other end of this intermediate and final prepolymer would be the same reaction product depicted above in structure I for the previous scheme, the di-sodium epoxide bisphenol A adduct, which is the first prepolymer product available in this particular epoxy system. Compared to the previous scheme, this approach reverses the orientation of attachment so that the alpha carbon in epoxide molecule combines with the phenoxy oxygen (rather than the epoxide carbon directly). Nevertheless, the epoxide group still includes the two terminal carbons, same as that in structure I.

Now, if less than a 2:1 ratio is utilized, a larger prepolymer can be obtained in a ring-opening process when structure I is attacked by the phenoxy intermediate and the two combine to give the second prepolymer product (after washing) which is comprised of two epoxy end caps and two bisphenol units linked by a third epoxide unit (formerly) which has been reduced to the corresponding alcohol. This incorporates pendant hydroxyl groups into the prepolymer . . .



As can be seen, the Stage A prepolymer in this scheme is larger than that depicted in the previous path leading to structure I. Also, note that the chloride groups are long gone from the system and do not participate in this phase of the process where the original NaOH catalyst is regenerated. The prepolymer or Stage A resin is often referred to as the 'neat' resin. Overall, this scenario leaves the ring intact during the initial part of the process (in contrast to the previous scheme) but involves opening of one of the terminal rings on the first reaction product to facilitate production of the larger prepolymer (the second, third and fourth reaction products may be more representative of industrial grade epoxy resins). It is well established that unreacted (residual) terminal epoxide groups (as well as pendant hydroxyl groups along the epoxy chain) are crucial in the formation of coupling links with functional groups across the surface of the various substrates epoxy resins are applied to (for instance, the carboxyl and hydroxyl groups along the surfaces of carbonized fibrous reinforcements). Also, it is crucial to ensure that all the sodium and chloride ions are completely washed out of the system before packaging of the resinous product (remnants of either of these ions in the neat resin product could wreak havoc on the aerospace industry with worldwide corrosion problems).

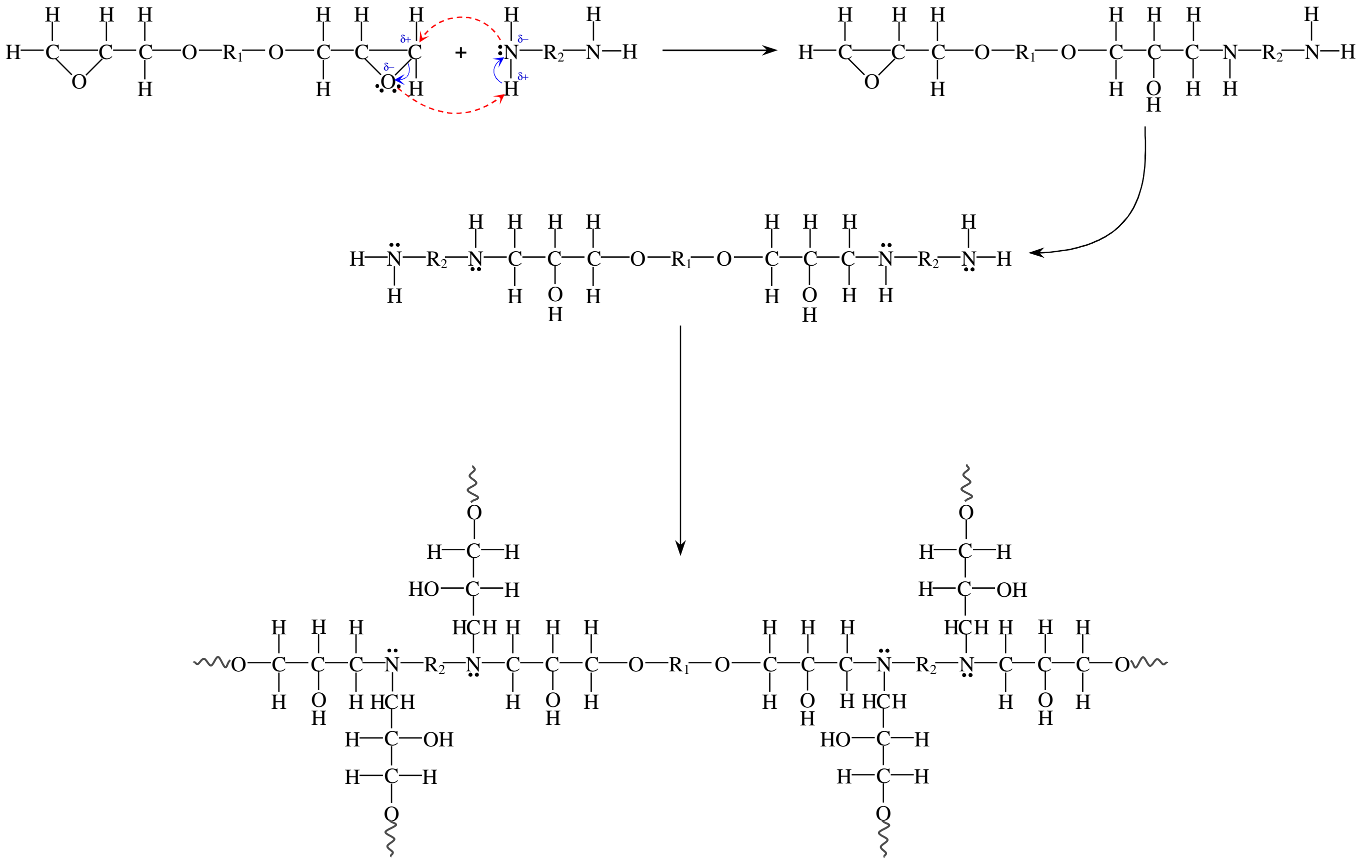
For familiar two-part 'room temperature' curing epoxy systems, this exemplifies the well known critical requirement that the 'Part A' and 'Part B' components in the epoxy kit (respectively, the epoxy prepolymer and the amine or anhydride crosslinker) be mixed together as precisely as possible in accordance with vendor recommendations. In single component heat-cured epoxy-based resins bound for the composite prepreg and coatings industries, these two components are precisely formulated and blended together by the resin manufacturer, but they do not interact until the end-user (composite manufacturer or coating applicator) applies the minimal amount of heat required to initiate crosslinking reactions (typically during autoclave or heat-applied curing). Thus, in single component epoxy systems, the prepolymer and crosslinker are essentially inert to one another at ambient (shop) conditions and do not react until a certain temperature is reached (corresponding to the activation energy), then the crosslinking process ‘kicks off’.

Section II: Resin Advancement

Throughout the industry, prepregs and epoxy-laden adherends containing the neat resin are often ‘staged’ by applying a low level of heat (well below the curing temperature) for a specific amount of time as an intermediate process step before subjecting the substrate to final curing (crosslinking) operations. The material may be placed in a air-circulating oven to perform this process or sometimes, skilled operators may use a heat gun to perform localized staging. Staging forms a minimal level of crosslinks and increases the viscosity of the resin. It is a well established practice and has been proven to provide several benefits, including but not limited to: (a) enhanced handlability during lay-ups and resin application, improving properties such as tack, debonding, springback and ply separation, (b) more uniform crosslinking during the final curing process, particularly for thick laminates and thick bondlines, sometimes precluding the negative effects of nonuniform curing within the article as reflected by differentials between leading and lagging thermocouples, and (c) reduced levels of resin bleed-out (or squeeze-out) during the final higher temperarure cure, which reduces resin loss, increases resin content amd minimizes waste. Thermoset resins treated in this manner are considered as Stage B.resins and the process is often referred to as ‘B-staging’. Eventually, the B-staged article is subjected to final heat curing operations (often as a vacuum bag assembly inside a pressurized autoclave) and converted to the hardened Stage C state which represents the final cured/crosslinked state of the thermosetting process. Typically, the particular autoclave curing process applied has been optimized beforehand to follow a specific time/temperature/pressure profile best suited for that resin relative to the structural requirements pertaining to the composite article or bonded joint.

Section III: Amine Crosslinking

Amine catalysts for epoxy resins come in various forms depending on the specific fabrication conditions employed, desired curing parameters and ultimate properties required, including primary, secondary, tertiary amines and diamines. ‘Part B’ products may consist of complex amino adducts which can contain plasticizers, fillers, wetting agents and several other constituents to influence processing properties and cured physical and mechanical attributes. Primary amines provide for greater crosslink density while substituted amines allow for custom property modification. Consider the crosslinking process involving a diamine with the prepolymer given in structure I. For brievity, let bisphenol A and the diamine be represented by the following simplified structures, respectively . . . $HO—R_1—OH$ and $H_2N—R_2—NH_2$, and then the crosslinking mechanism between structure I and the diamine might be is given as . . .



crosslinked epoxy network