Chapter I

Introduction

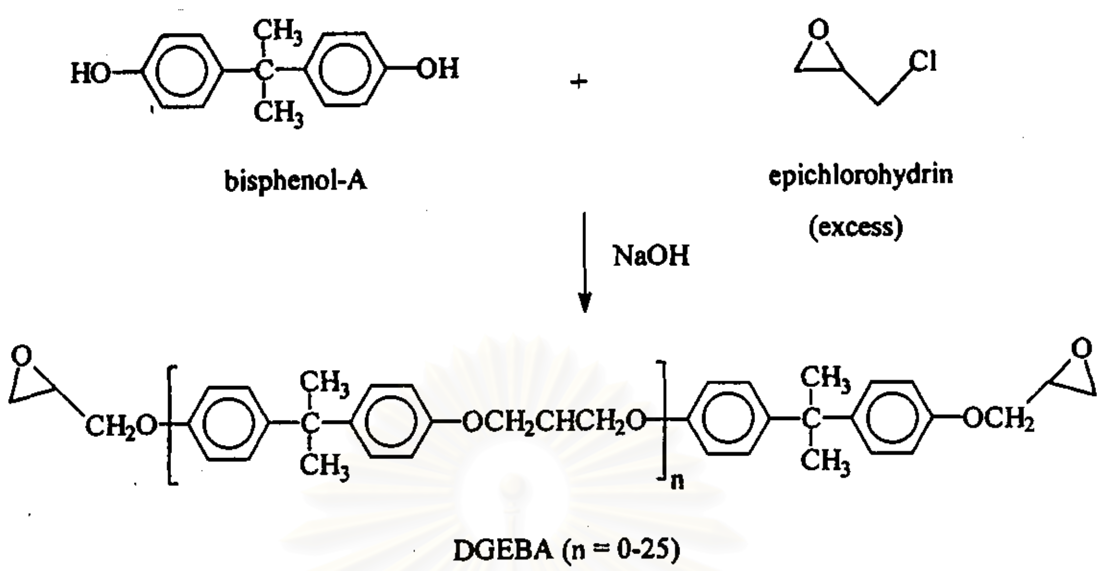
1.1 Epoxy resin

Since the invention and discovery of epoxy resin in the late 1930's by Castan and Greenlee, the production of epoxy resin has grown steadily.[1,2] Until now, epoxy resin consumption cannot be compared with thermoplastic materials that are used annually but it possesses various application and unique complexity of science and technology.

Studies of the resins include the nature of the resins and the ways they crosslink, possibilities in compounding and applying the resin in different uses. Crosslinked epoxy polymers have unique useful properties such as low shrinkage, high adhesive strength, high electrical insulation, good chemical resistant and also good mechanical properties. Examples of application for epoxy resins are adhesive bonding, construction materials, composites, laminates, coating, molding, textile finishing air and spacecraft industries.[3,4]

The most commercially important epoxide resins are prepared by the reaction of bisphenol-A with epichlorohydrin in the presence of sodium hydroxide. The reaction produces diglycidyl ether of bisphenol-A (DGEBA) as shown in Scheme 1.1[5,7]

The value of n determines the applications of DGEBA. The resin is liquid when $n < 1$ and solid when $n > 2$. The n value of low molecular weight liquid DGEBA is about 1 or less. When $n = 0$, The resin is known as monomeric DGEBA.[3]



Scheme 1.1 Synthesis of diglycidyl ether of bisphenol-A (DGEBA)[3]

1.2 Crosslinking Reactions[5]

The crosslinking reaction of epoxy resins may be carried out through the various functional groups existing in the molecular chain. The study of the crosslinking mechanism of DGEBA has shown that the crosslinking may be occurred either through the epoxy groups or the hydroxyl groups of DGEBA. The chemistry of crosslinking is complex depending on types of crosslinking agents or hardeners. The most common crosslinking agents are amines.

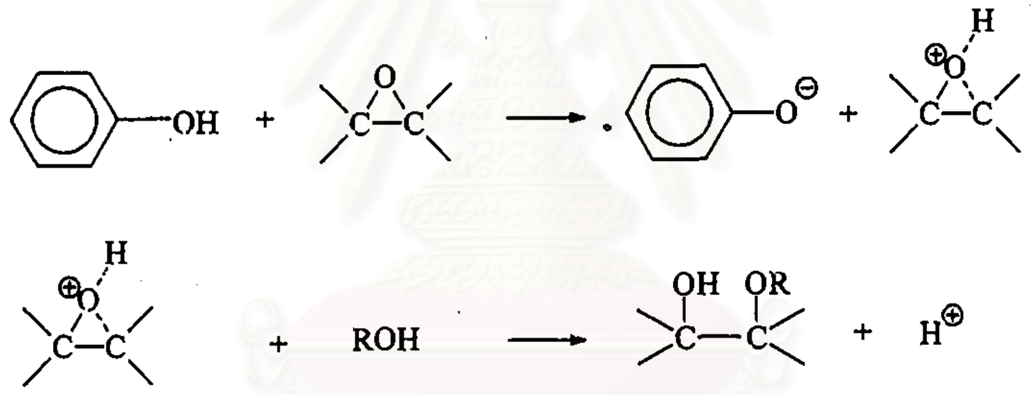
1.2.1 Amine Crosslinking Agents[8,9]

Amine is an important crosslinking agent for epoxy resins and can be divided into aliphatic amines, cycloaliphatic and tertiary aliphatic amines, and aromatics amines.

The reaction of DGEBA with amine can occur by the reaction between the amine group and epoxide group. The crosslinking reaction depends on the number of amino hydrogen on crosslinking agent, reactivity of crosslinking agent, the number of epoxide groups in DGEBA. These factors result in different physical and mechanical properties of the final products.

1.2.2 Phenolic Crosslinking Agents[5]

One type of crosslinking agents used in industrial is phenolic compound. Some phenolic crosslinking agent such as diphenol crosslinked with epoxidized olefin resin at high temperature to produce high molecular weight DGEBA. The exact mechanism have not been studied. A possible route is part of the reaction proceeds through the formation of an oxonium ion intermediate as shown in Scheme 1.2.



Scheme 1.2 Possible mechanism of crosslinking reaction of DGEBA with phenol

There are many researches about phenol as crosslinking agent, for example, crosslinking reaction between phenol and phenyl glycidyl ether by using and without using catalysts.[10] Without catalyst, it was found that the reaction occurred at 200^{0}C. About 60% of the reaction was epoxide with phenol and 40% of the reaction was epoxide with alcohol as shown in Figure 1.1

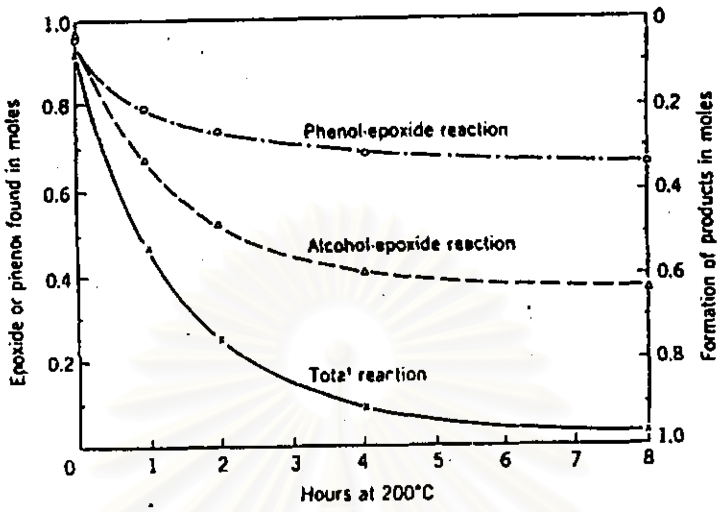


Figure 1.1 The reaction between phenol and phenyl glycidyl ether when no catalyst was used[10]

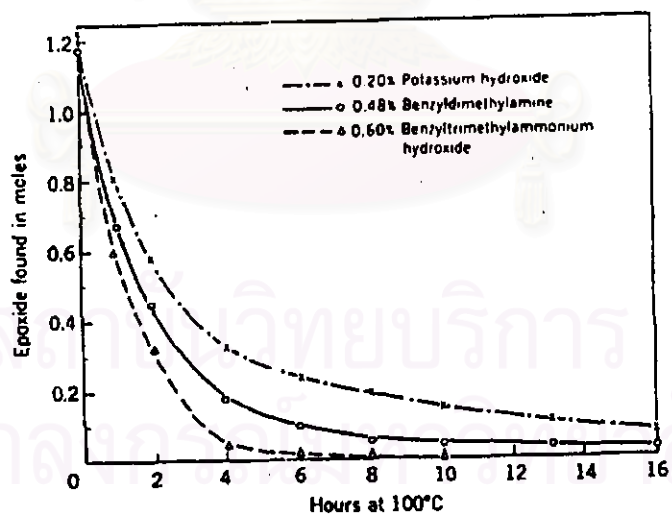
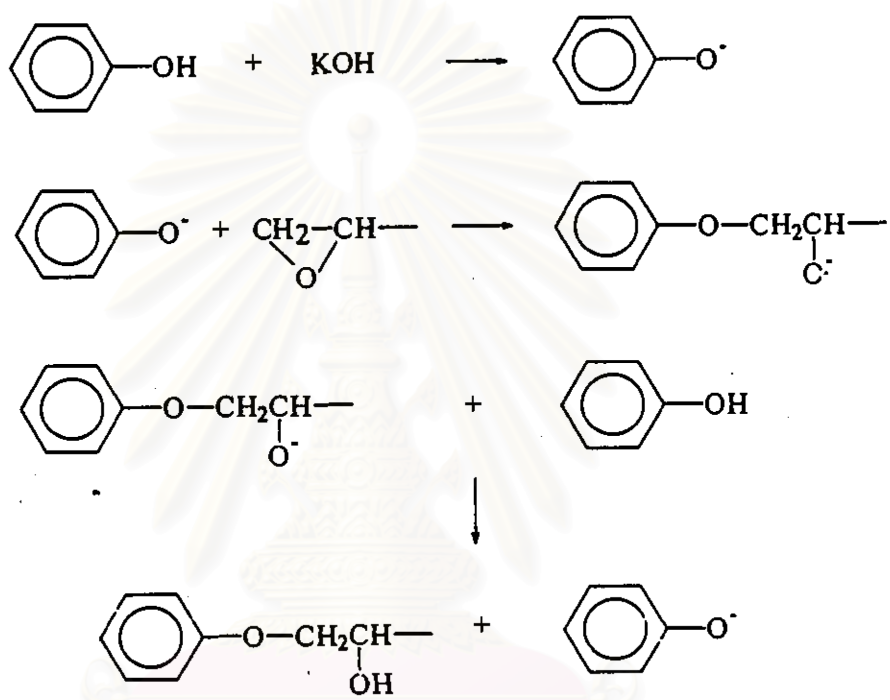


Figure 1.2 The reaction between phenol and phenyl glycidyl ether when the catalyst was used[10]

As shown in Figure 1.2. The base-catalyzed reaction proceeded at 100^0C almost exclusively by phenol-epoxide route, without alcohol-epoxide reaction. The role of tertiary amines as catalysts for the reaction was also examined and it was observed that benzyldimethylamine was a more effective catalyst than potassium hydroxide, and benzyltrimethyl ammonium hydroxide was even more powerful. Shechter and Wynstra propose the mechanism as shown in Scheme 1.3



Scheme 1.3 Possible mechanism of the reaction between phenol and phenyl glycidyl ether when using KOH as a catalyst[10]

First, phenol is ionized to phenoxide ion by potassium hydroxide. The phenoxide ion then attacks epoxide to give alkoxide ion which reacts immediately with the phenol present in excess to regenerate the other phenoxide ion.

1.3 Metal-containing epoxy polymers

One alternative to improve the properties of epoxy polymer was to synthesis metal-containing epoxy polymers. This resulted in the improvement of mechanical strength, chemical resistant, adhesive strength and thermal stability.

There are two main directions of the improvement of the epoxy polymer properties by introduction of metals into the polymer matrices.[11] These are the polymerization of the homogeneous or of the heterogeneous metal-containing epoxy compositions. The heterogeneous epoxy systems have metal atoms as the particles of modifying mixtures while the homogeneous systems, the metal atom bond with the other atoms of polymer chains by chemical linkage. The latter gives the highest stabilizing effect.

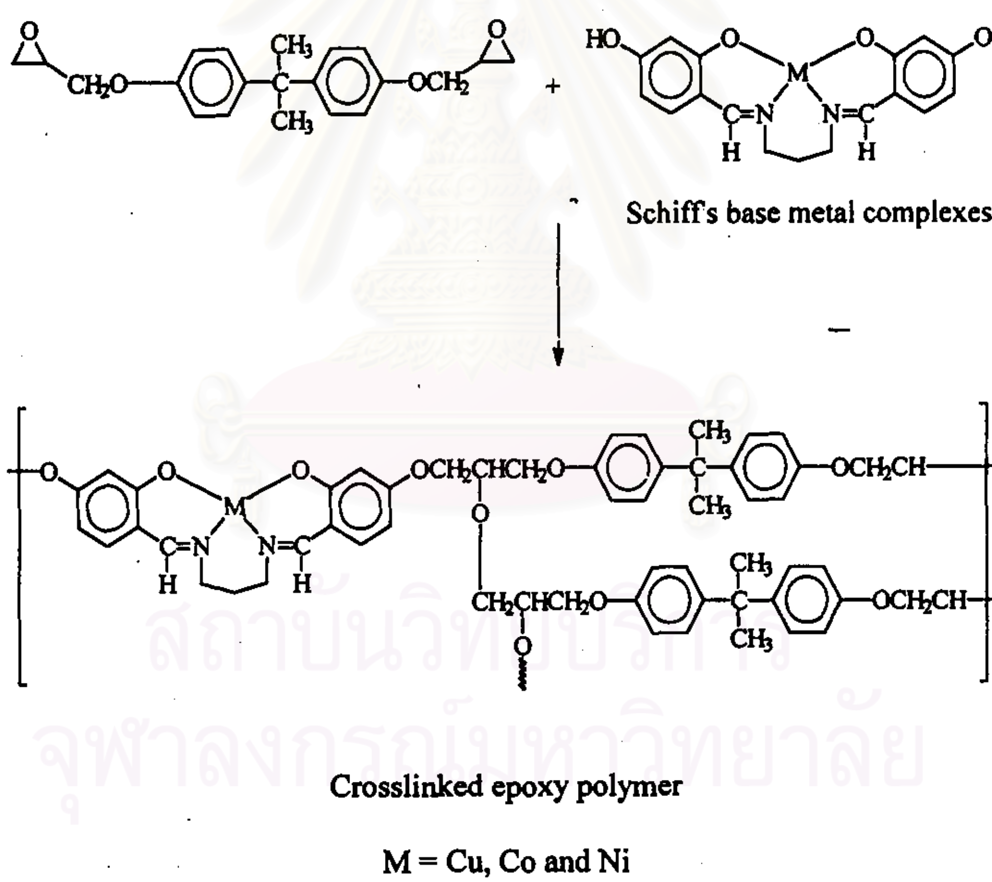
The presence of the metal in the polymer chains increases mechanical strength or deflection temperature of polymers. Metal-containing epoxy polymers in homogeneous system can be obtained by using metal-containing oligomers and metal-containing epoxy hardeners. An example of metal-containing oligomers is obtained from the reaction of epichlorohydrin with hydroxy naphthylselenide[12] to give the epoxy compound. After hardening with polyamine, it gives tensile strength of 90 MPa and adhesive strength of 11 MPa and deflection temperature of 130^{0}C.

There are many works involving metal-containing epoxy polymers. In 1992, Anand and Srivastava[13,14] had synthesized epoxy resin containing chromium, copper and zinc. The obtained polymers possessed better thermal stability, chemical resistant and electrical conductivity than ordinary epoxy polymers without metal in their structures.

Crosslinking of DGEBA with tetradentate and hexadentate transition metal complexes was studied by Kurnoskin.[15-24] One example is a complex of the metal salt of copper with aliphatic amine [Cu(R) (HOC6H4COO)n] where n = 2 and R = bis-N,N-(β-cyanoethyl)-

diethylenetriamine.[24] Crosslinking of DGEBA with this metal complex gave the polymer with deflection temperature of 115^{0}C, tensile strength of 90 MPa and 3.0% weight loss after treatment in air for 100 h at 260^{0}C. The epoxy compositions chelate of $Cu(o\text{-}C_6H_4(NH_2)_2(HOC_6H_4COO)_2$ were used to produce one-glass plate glass-reinforced plastic springs for large loaded motor vehicles.[25]

Synthesis of metal-containing epoxy polymers could also be done by using Schiff's base metal complexes as crosslinking agents for DGEBA (Scheme 1.4).[26] The polymers showed good thermal resistance and high T_g values.

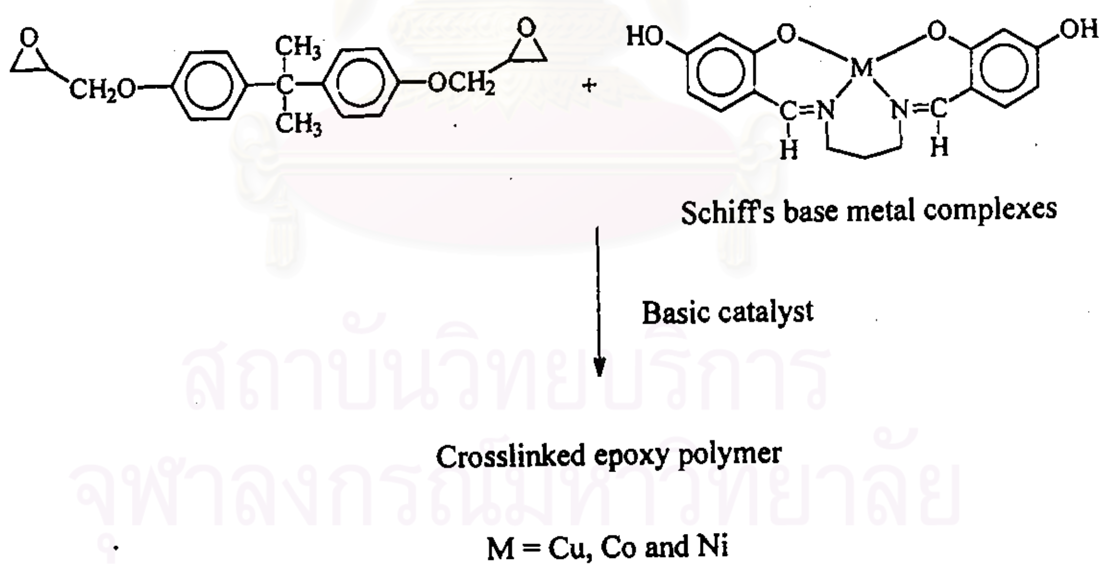


Scheme 1.4 Synthesis of metal-containing epoxy polymers[26]

It was found that the crosslinking reaction of DGEBA with Schiff's base metal complexes occurred at high temperature. This brings about inconvenient for further work. Therefore, the use of catalyst to reduce crosslinking temperature was studied in this work.

1.4 Objective and Scope of the Research

The objective of this work was to synthesize metal-containing epoxy polymers by using basic catalysts such as amine, NaOH and quaternary ammonium salt in order to decrease the crosslinking temperatures (Scheme 1.5). The crosslinking reaction was also expected to be more complete which should result in better thermal and mechanical properties of the polymers. Finally, study of the optimum conditions for crosslinking reaction was done, thermal properties and mechanical properties of the metal-containing epoxy polymers were investigated.



Scheme 1.5 Synthesis of metal-containing epoxy polymers by using of catalyst