CHAPTER I

INTRODUCTION

1.1 Heat-resistant Polymers

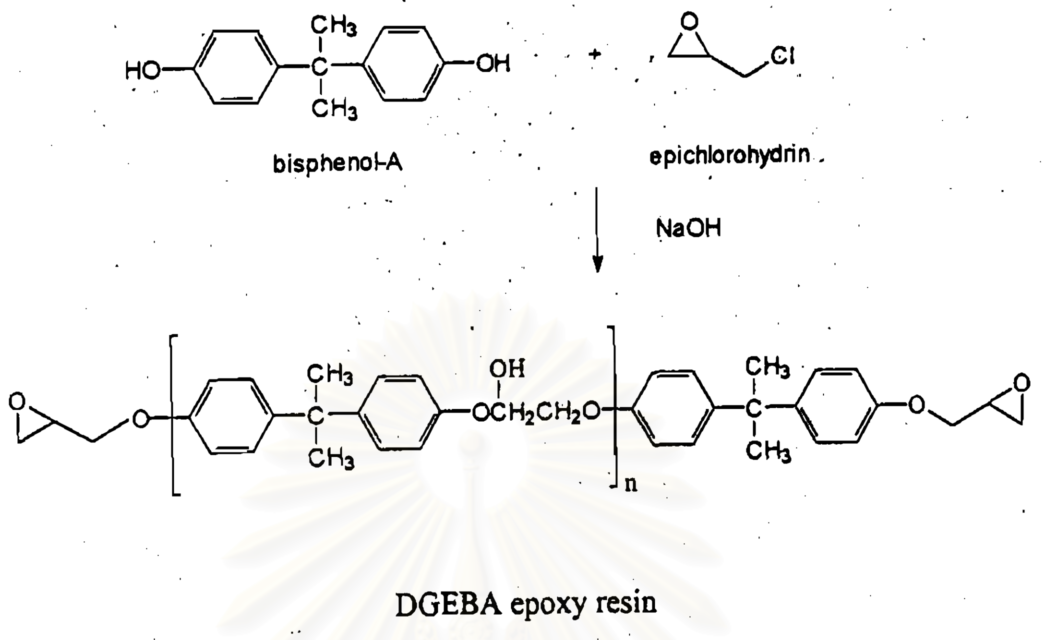
One of the driving forces in polymer synthesis is the search for polymers to replace metals since polymers are lightweight and easy to process into required shapes. One of the major synthetic efforts since the late 1950s is in the area of high-temperature polymers or heat-resistant polymers.[1-3]

Heat-resistant polymers are high-performance polymers that can be used at high temperatures. The need of such polymers is their potential application in many areas such as aircraft, spacecraft, automotive and electronic components. Polymers with high strength, solvent and chemical resistance and stability at temperatures higher than 250^{0}C would be very useful.

Organometallic polymers have been studied in development of heat-resistant polymers. The general synthetic method is the introduction of metal atoms into polymer chains by the linkage between metal atoms and heteroatoms in polymer chains. Organometallic polymers containing metal atoms bonded by coordination such as metal complex systems are known as coordination polymers. Polymerization may involve metals as reaction centers or may not concern metal centers at all.

1.2 Epoxy Polymers

Epoxy resins have molecules containing more than one α - epoxide group[4] capable of being converted to a useful thermoset form. Epoxy resins are prepared commercially by the reaction between epichlorohydrin and bisphenol-A in the presence of sodium hydroxide (Scheme 1.1).



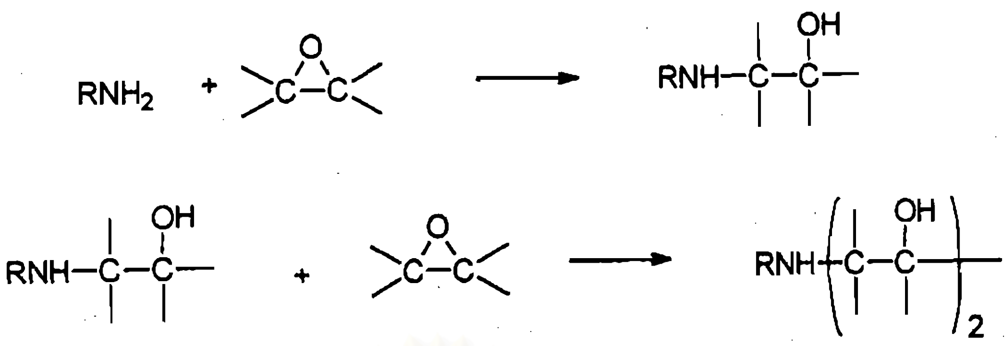
Scheme 1.1. Synthesis of epoxy resin

The reaction gave the diglycidyl ether of bisphenol – A (DGEBA). The low-molecular-weight liquid products have an n value about 1 or below; when n=0 , the resin is known as monomeric DGEBA. Upon mixing epoxy resin with a proper crosslinking agent, the resin can be converted into a thermoset epoxy polymer.

Crosslinked epoxy polymers have useful properties such as low shrinkage, high adhesive strength, good mechanical properties, high electrical insulation, and good chemical resistance. Therefore, they offer wide applications in the areas of aircraft, automobile and coating industries.

1.2.1 Aliphatic Amines Crosslinking Agents

The polyamines (primary, mixed primary and secondary and combinations of these with tertiary amines) are useful crosslinking crosslinking agents. The crosslinking reaction between amines and DGEBA is shown in Scheme 1.2.



Scheme 1.2. Crosslinking reaction of DGEBA with amine

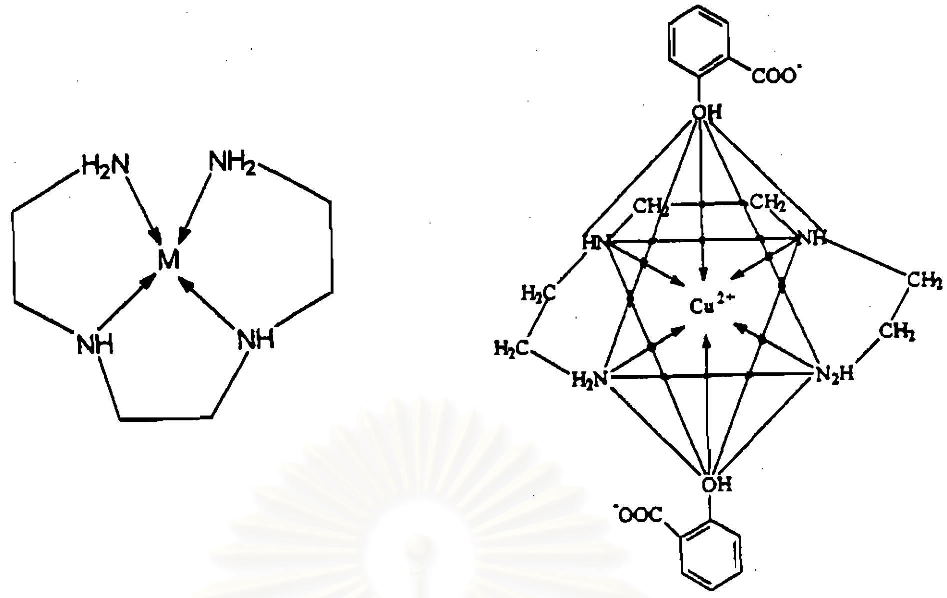
1.3 Metal-Containing Epoxy Polymers

Attempts have been made to improve physical and mechanical properties of epoxy polymers. Currently, metal-containing epoxy polymers[5] can be obtained by crosslinking of epoxy resin in the presence of metal complexes.

Anand and Srivastava synthesized epoxy resins containing zinc, chromium and copper by reacting acrylate salts with bisphenol–A and excess epichlorihydrin followed by cureing with polyamide[6-8].

The modified epoxy resins containing transition metals have superior properties of chemical resistance, thermal resistance and electrical conductivity than the unmodified epoxy resins. The explanation for the experimental results is the assumption that the metals form complexes with oxygen atom in the epoxy resin.

Kurnoskin prepared metal-containing epoxy polymers by crosslinking DGEBA with the complexes of first row transition metals and aliphatic amines. Some examples of metal complexes are shown in Figure 1.1[9-16].



[M(trien)] [M(trien)($HOC_6H_4COO)_2$]

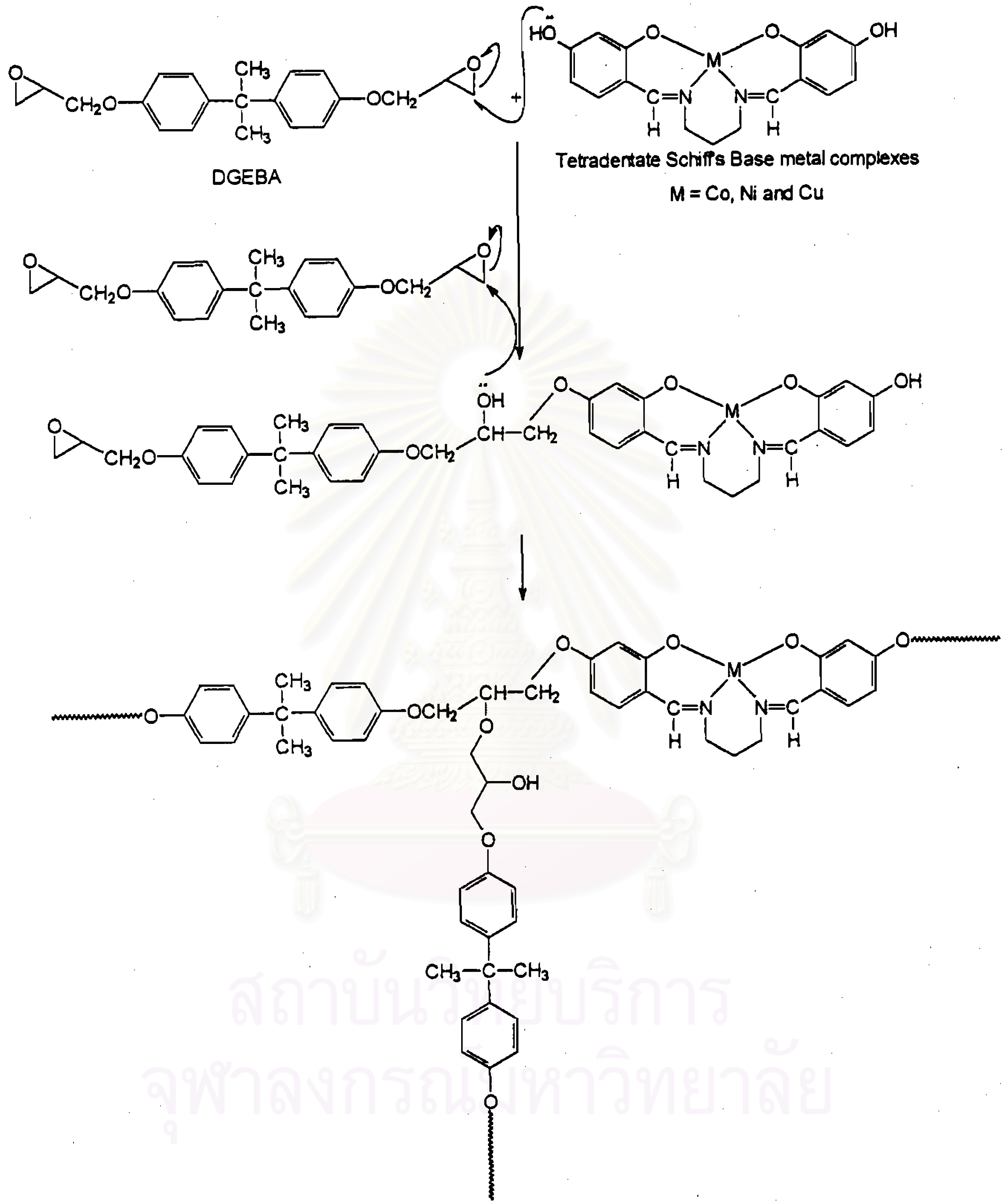
M = Zn, Cu, Ni, Co, Fe, Mn

Figure 1.1. Structure of metal complexes of first transition metal

The metal-containing epoxy polymers have good thermal oxidative stability, chemical resistance, electrical resistance and high strength. For example, the epoxy matrices increases the deformation temperature (DT) up to 163 ^{0}C and tensile strength up to 100 Mpa.

Lin, Shu and Wey investigated the toughening effects of $Cr(acac)_3$ as an additive to the DGEBA/diethylenetriamine system[17-20]. The results have been further supported by wide-angle x-ray scattering analyses, which revealed that $Cr(acac)_3$ could interact with hydroxy groups in the epoxy networks and reinforce the structure. It was also believed that this interaction shortened the repeat distance of local ordered structure in the crosslinked epoxy network.

Tongraung synthesized metal-containing epoxy polymers[21]. Crosslinking of DGEBA was done using tetradentate Schiff's base metal complexes of cobalt, nickel and copper as crosslinking agents. These Schiff's base metal complexes have two phenolic groups which are able to react with DGEBA to give epoxy polymers. A likely mechanism of the crosslinking reaction is shown in Scheme 1.3.



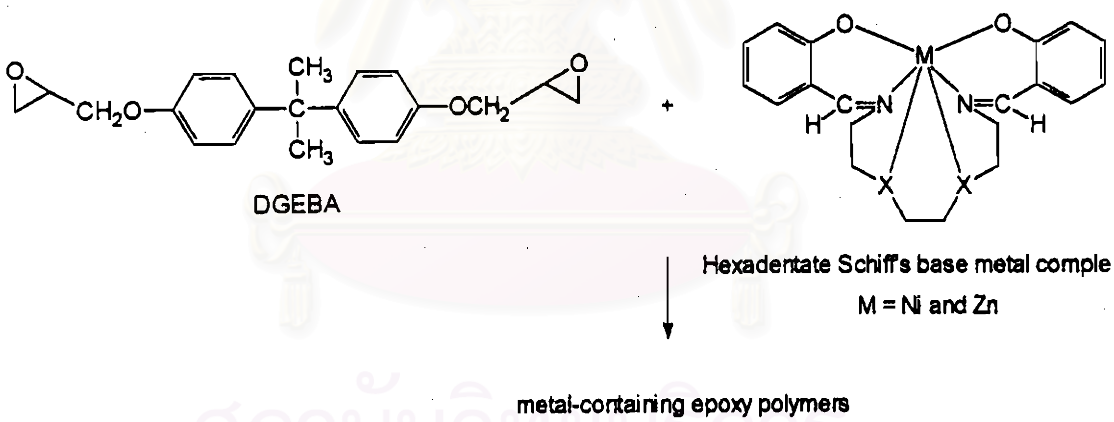
Metal-containing epoxy polymer

Scheme 1.3. Possible mechanism of the reaction of tetradentate Schiff's base metal complexes with DGEBA

The resulting metal-containing epoxy polymers had good properties and thermal stability. However, the Schiff's base metal complexes were not soluble in organic solvents; therefore, mold casting of the epoxy polymer is quite difficult.

1.4 Objective and Scope of the Research

In our work, efforts were made to synthesize metal-containing epoxy polymers since it was known that addition of metals into polymer network to improves thermal properties, physical properties and curing speed of polymers. Crosslinking of DGEBA was done by using hexadentate Schiff's base metal complexes as crosslinking agents for DGEBA (Scheme 1.4). The optimum conditions for the crosslinking process were studied. Thermal properties and mechanical properties of the metal-containing epoxy polymers were then investigated.



Scheme 1.4. Synthesis of metal-containing epoxy polymers.