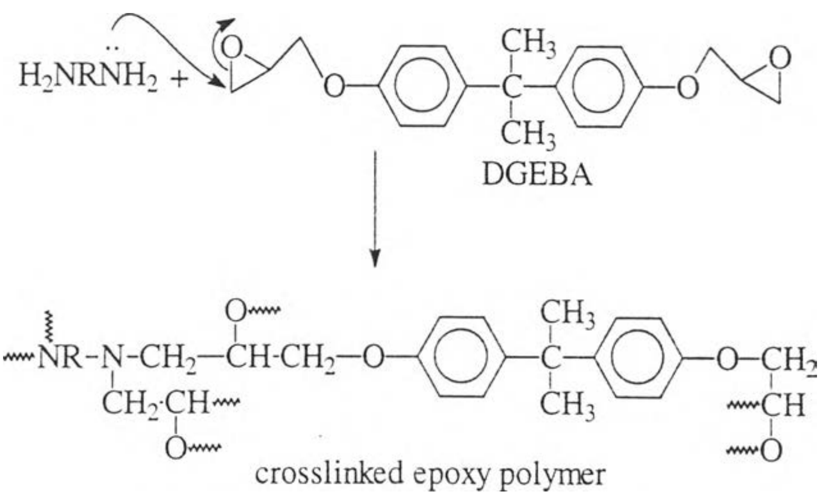
CHAPTER I

INTRODUCTION

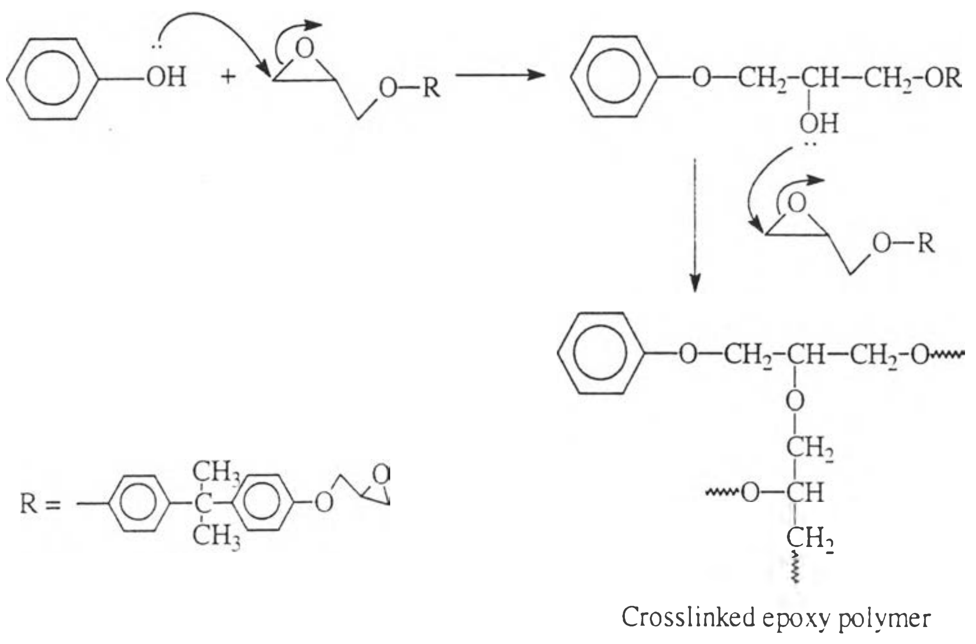
1.1 Epoxy Polymers

Epoxy polymer is one of the most important nonvinyl polymers. They represent a special type of polyether obtained by crosslinking of diglycidyl ether of bisphenol-A (DGEBA) epoxy resin with proper crosslinking agents such as amines, phenols, organic acids and carboxylic acid anhydrides.[1-5] For example, amines react by nucleophilic addition to the epoxide ring to give crosslinked epoxy polymers as shown in Scheme 1.1.



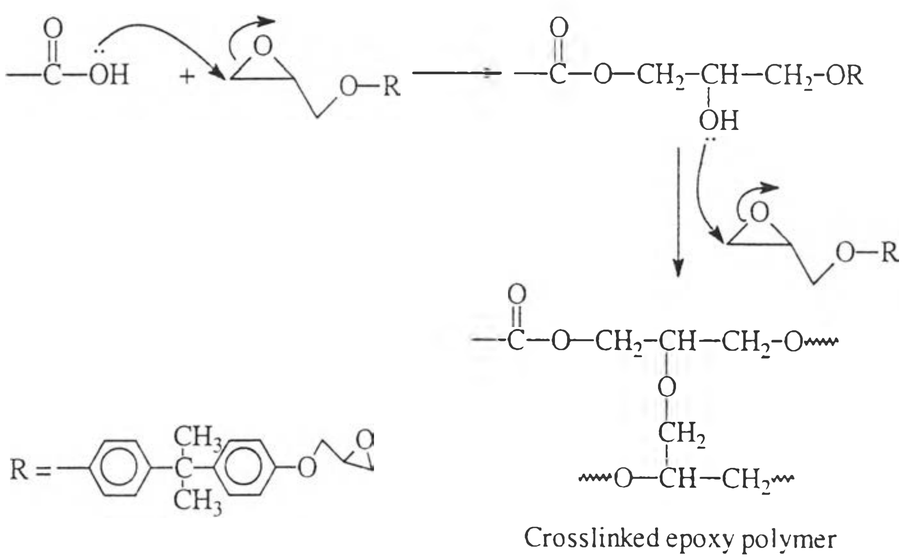
Scheme 1.1 Crosslinking reaction of DGEBA with amine

Phenols react with epoxy resins at elevated temperatures. The possible mechanism is shown in Scheme 1.2.



Scheme 1.2 Crosslinking reaction of DGEBA with phenol

For organic acid, the initial crosslinking reaction is epoxide ring opening as shown in Scheme 1.3. The formed alcoholic hydroxyl then reacts with DGEBA.

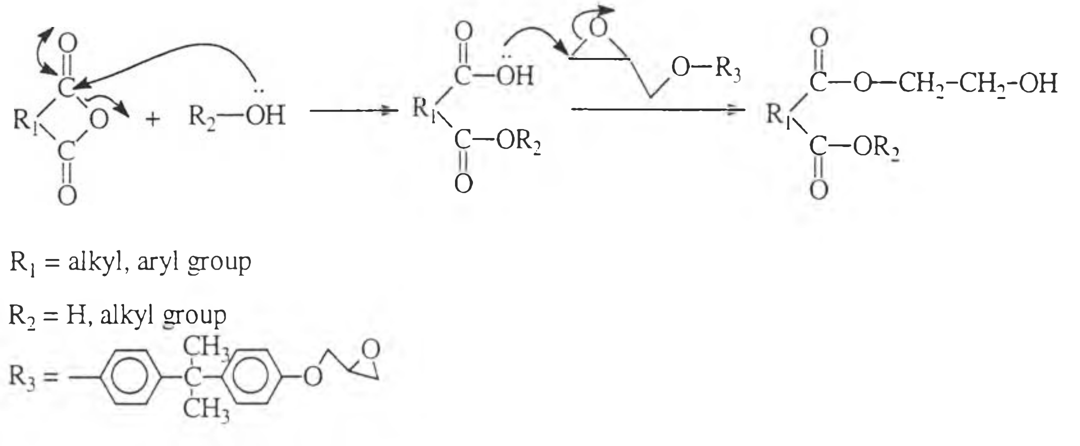


Scheme 1.3 Crosslinking reaction of DGEBA with organic acid

1.2 Acid Anhydride Crosslinking Agents

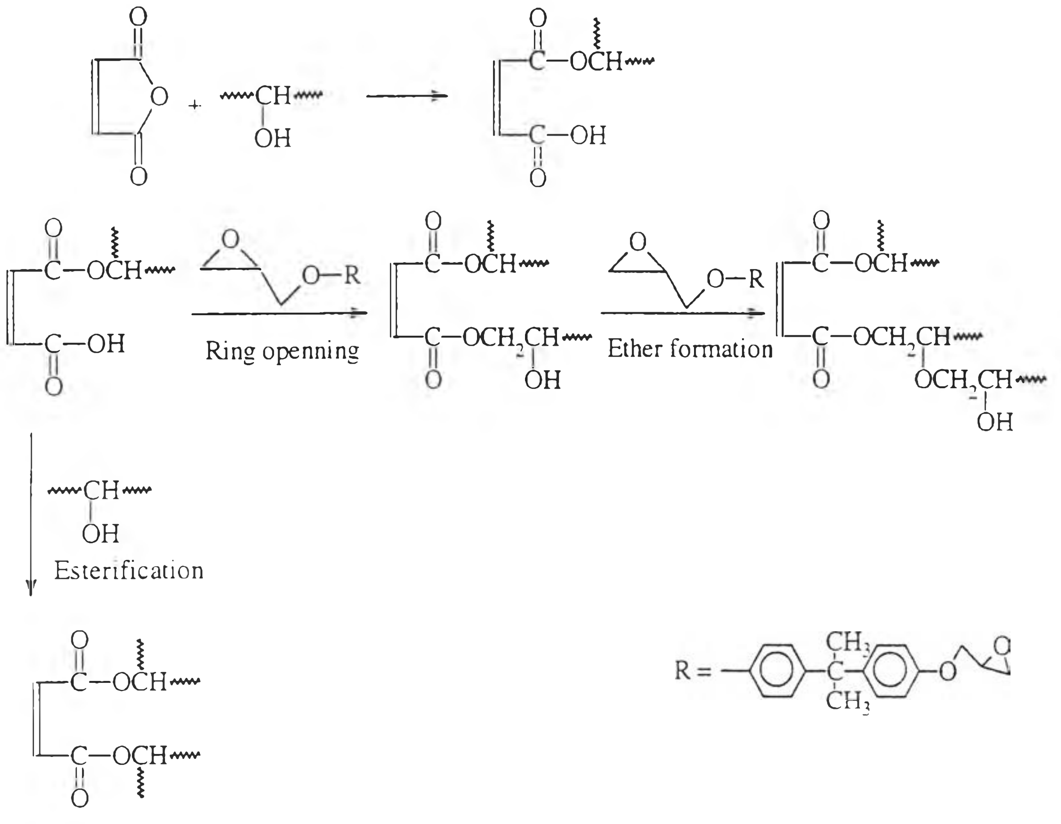
One type of crosslinking agents used industrially in crosslinking reaction of DGEBA is acid anhydride.[6,7] They offer excellent properties of epoxy resin such as good thermal, electrical properties, and long useful pot lives. In the absence of accelerator, the anhydride can not react with epoxy groups. The anhydride ring may be opened either by acid accelerators such as water or alcohols, or by basic accelerators such as amines.

A ring opening of an anhydride by water or an alcohol (Scheme 1.4) produces a carboxyl group which can then open an epoxide rings to generate a hydroxyl group which undergo further polymerization.



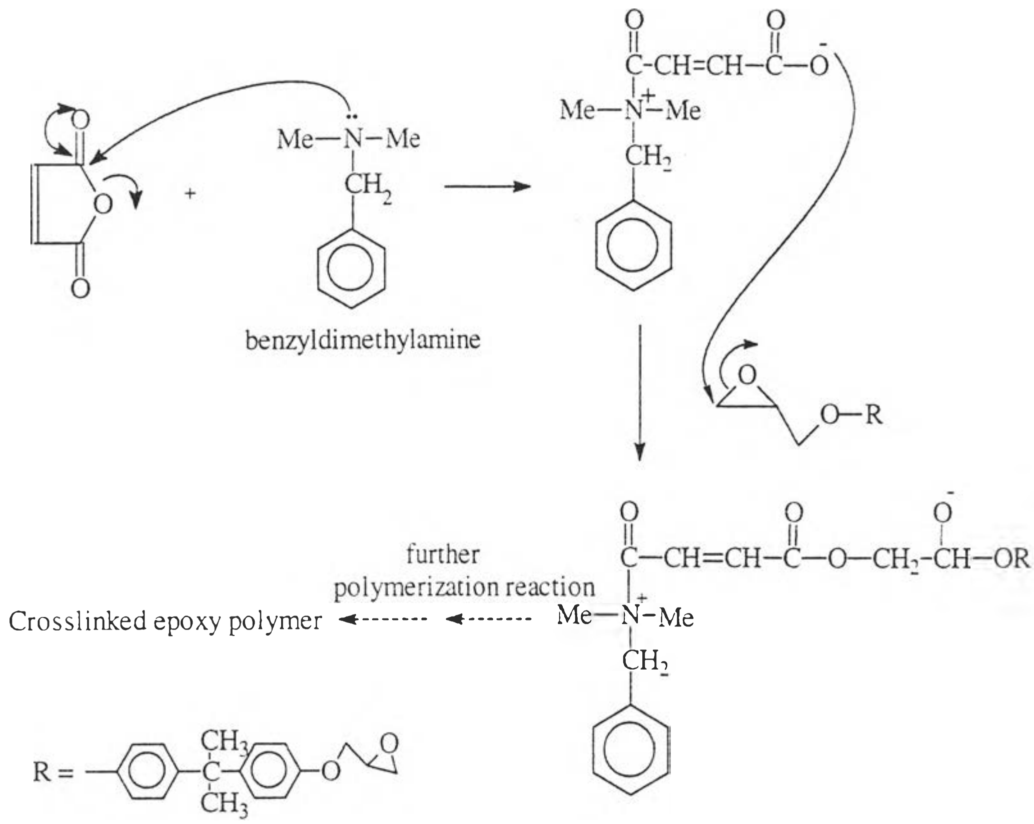
Scheme 1.4 Ring opening of acid anhydride by alcoholic accelerators

For example, maleic anhydride reacts with an alcohol to give ester acids. The carboxyl groups can then open the epoxide rings or react with other hydroxyl groups to form more ester groups. The acid catalyzed reaction between hydroxyl and epoxide groups can also produce ether linkages (Scheme 1.5).



Scheme 1.5 Possible mechanism of the crosslinking reaction of DGEBA with maleic anhydride in the presence of alcohol

Many basic accelerators for anhydride cures are available such as tertiary amines. The preferred tertiary amines are benzyldimethylamine and tris(dimethyl-aminomethyl)phenol. The amount employed usually in the range of 1-5 phr. The possible mechanism of the reaction between DGEBA and maleic anhydride in the presence of benzyldimethylamine is shown in Scheme 1.6.



Scheme 1.6 Mechanism of the reaction between DGEBA and maleic anhydride in the presence of benzyldimethylamine

1.3 Metal-Containing Epoxy Polymers

The development of electronics and the aerospace industry demands the use of polymers with high mechanical strength and elevated thermal resistance. Metal-containing epoxy polymers have been shown to have high chemical resistance, good heat resistant and electrical properties as well as the very high adhesive strength.[5]

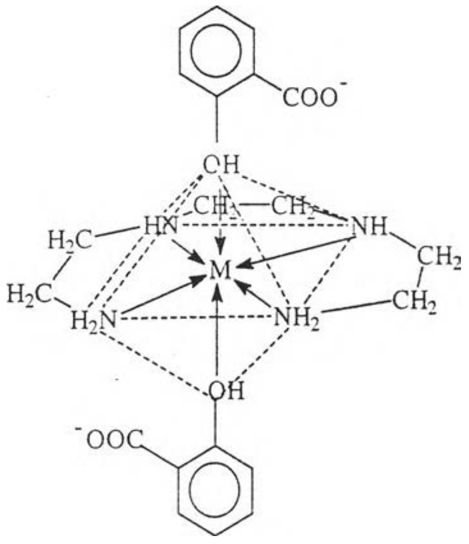
There are two usual approaches to introduce metal atom into the epoxy polymer matrix.[8] The first approach is to have metal atoms as structural fragments of the particles of the hardeners which bind the polymer matrix by physical nature. The other approaches is to have metal atoms presented in the constitutional units of the polymer matrix which bond with the other atoms of the polymer chains by chemical linkages.

An addition of mechanical strength and thermal resistance to epoxy polymers can be achieved as a result of the development of metal-containing epoxy polymers. These polymers are lightweight and easy to process into the required shape. The obtained properties depend on the metal types, the metal complex structure, the concentration of metal complexes in the polymer composition and the methods of introduction of the metal atoms into the epoxy polymer matrix.

In 1992, Lin, Shu and Wey[9,10] synthesized crosslinked epoxy polymers with organotransition metal complexes. Crosslinking of DGEBA was done by using diethylenetriamine in the presence of chromium and cobalt acetylacetonate as additives. The result showed that both metal complexes showed catalytic effect in crosslinking reaction by decreasing crosslinking temperature and were able to interact with hydroxy groups in DGEBA and reinforcing the epoxy network.

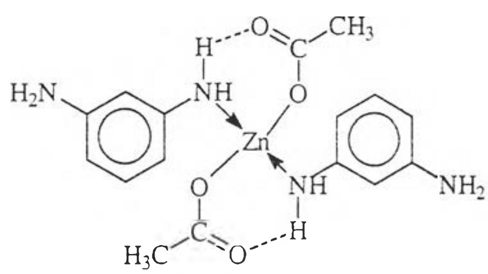
In the same year, Anand and Srivastava[11,12] synthesized epoxy resins containing zinc, chromium, copper and arsenic by reacting acrylates of these metals with bisphenol-A and excess epichlorohydrin. The resins cured with polyamide have improved thermal stability, chemical resistant and electrical conductivity as compared to conventional epoxy polymers without metals in their structures.

Kurnoskin[13-21] crosslinked DGEBA with tetradentate and hexadentate transition metal complexes. Examples of such metal complexes are shown in Scheme 1.7.

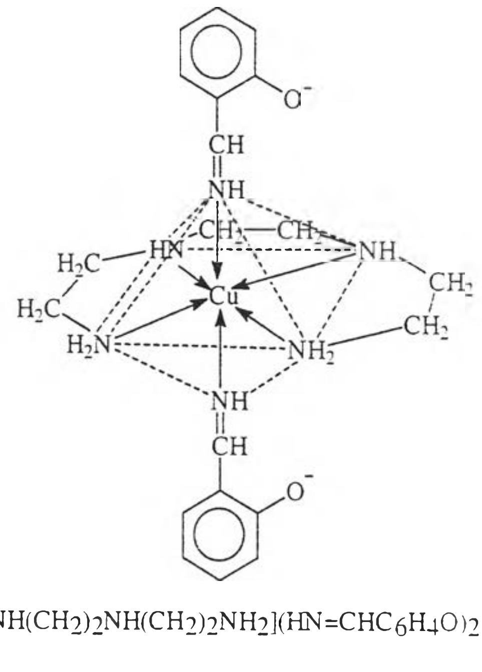


$M[H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2](HOC_6H_4COO)_2$

M = Cu, Co, Zn, Ni, Mn



$Zn(m\text{-}C_6H_4(NH_2)_2(CH_3COO)_2$

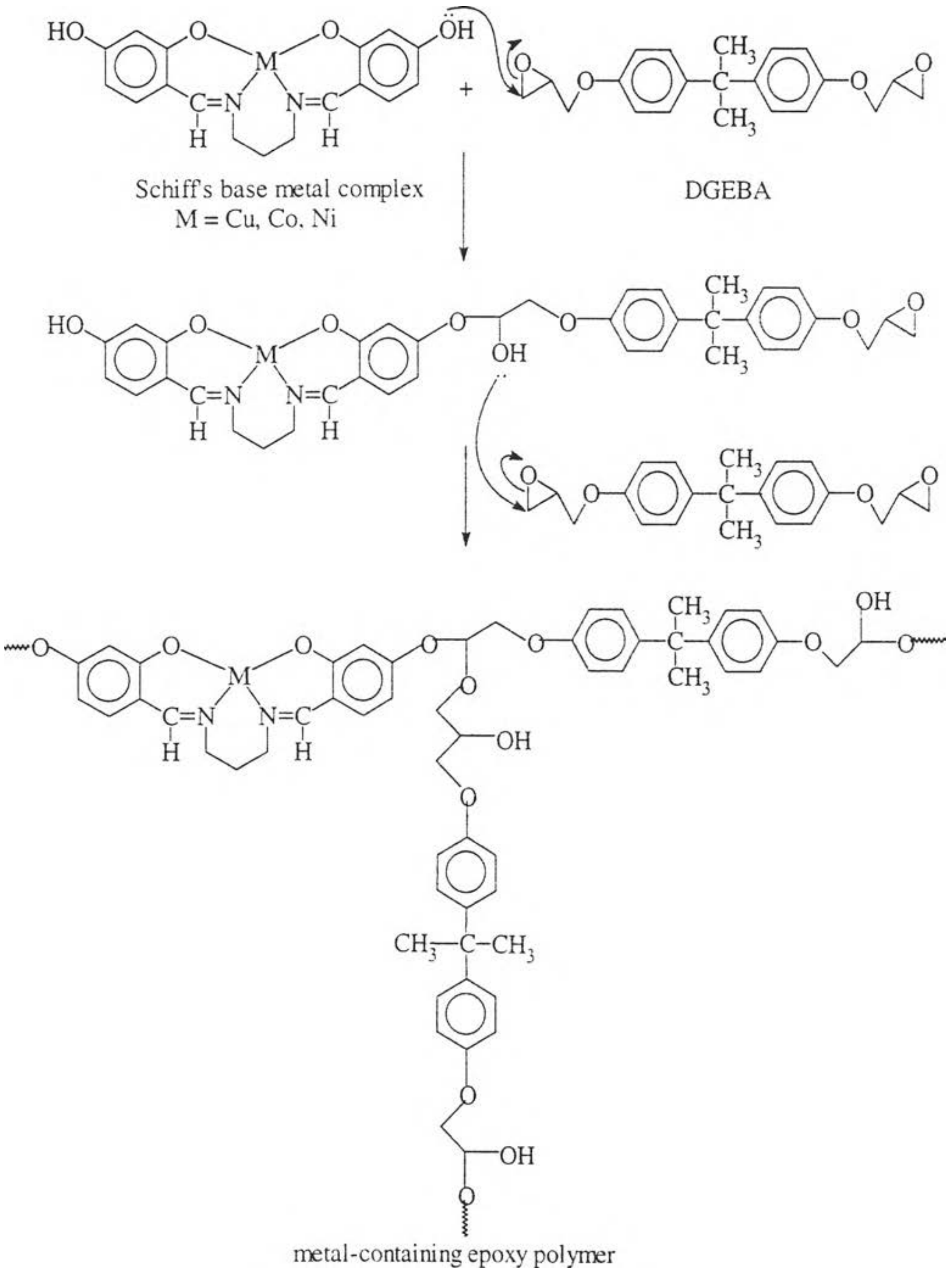


$Cu[H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2](HN{=}CHC_6H_4O)_2$

Scheme 1.7 Examples of metal complexes in Kurnoskin's work[14,15]

The metal-containing epoxy polymers showed good processibility, high-strength and high thermal resistance. Espectially, Zn-containing epoxy polymer obtained from $Zn(CN(CH_2)_2[NH(CH_2)_2]_3CN)(CH_3COO)_2$[21] had good thermal properties with deflection temperature (DT) at 130 °C and the value of mass loss of polymer after thermal treatment for 100 hours at 250 °C in air at 4.7%.

In 1997, Tongraung[22] synthesized metal-containing epoxy polymers to improve their thermal properties. Crosslinking of DGEBA was achieved by using tetradentate Schiff's base metal complexes as crosslinking agents as shown in Scheme 1.8.

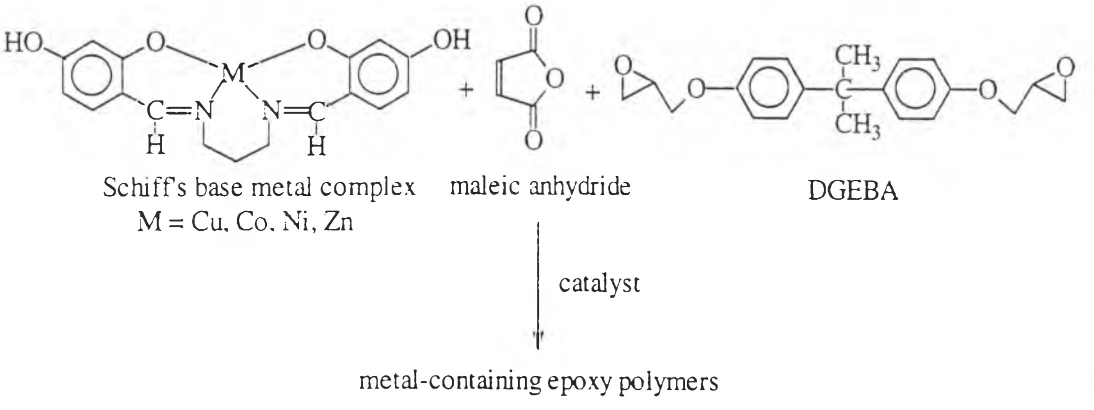


Scheme 1.8 Synthesis of metal-containing epoxy polymers using tetradentate Schiff's base metal complexes

However, high crosslinking temperature (190-240 °C) was required for copper, cobalt and nickel complexes. Crosslinking of DGEBA with zinc complex was not possible since the reaction occurred at higher temperature (350°C).

1.4 **Objectives and Scope of the Research**

This study concerned the synthesis of the heat resistant metal-containing epoxy polymers using low crosslinking temperature. This was done by crosslinking of DGEBA with tetradentate Schiff's base metal complexes in the presence of maleic anhydride and a basic catalyst (Scheme 1.9). Maleic anhydride was chosen due to the low melting point, low viscosity and high compatibility with DGEBA besides their ease of handling and less irritating to the skin. The metal complexes used are the same as those used in Tongraung's research. The presence of maleic anhydride and a basic catalyst was expected to cause a decrease in crosslinking temperature. Physical and mechanical properties of the metal-containing epoxy polymers were then investigated.



Scheme 1.9 Synthesis of metal-containing epoxy polymers using metal complexes and maleic anhydride as crosslinking agents