

CHAPTER II

LITERATURE SURVEY

2.1 Benzoxazine

Traditional phenolic materials are the crosslinked products of their low molecular weight precursors, either of novolac or resole type. The materials exhibit good heat-resistant, flame retardant and dielectric properties, however, there are a number of shortcomings, such as brittleness of materials, release of by-products during the curing process due to the condensation reactions, use of strong acid or base catalyst. Thus, the revitalization of phenolic materials with high-performance composite and electronic applications depends on the ability to create new chemistry and process to overcome the aforementioned shortcomings.

The novel phenolic resins, benzoxazines, were first synthesized by Holly and Cope (1944) from primary amine, formaldehyde, and phenol derivatives. The reaction of benzoxazine synthesis is shown in figure 2.1.

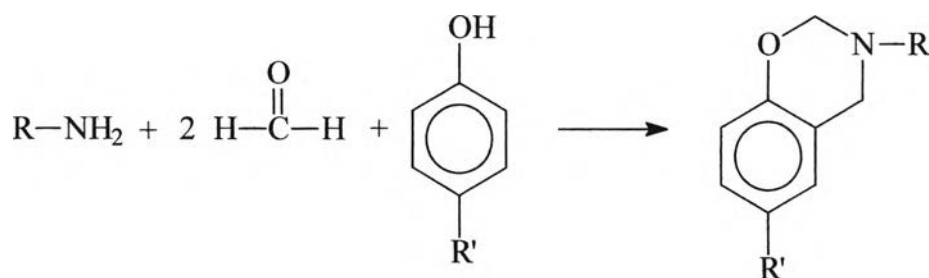


Figure 2.1 The reaction of benzoxazine synthesis.

Burke *et al.* (1949) found that benzoxazine rings react preferentially with the ortho position of free phenolic compounds to form a dimer with methylene-amine-methylene bridge structure. The curing reaction is shown in figure 2.2.

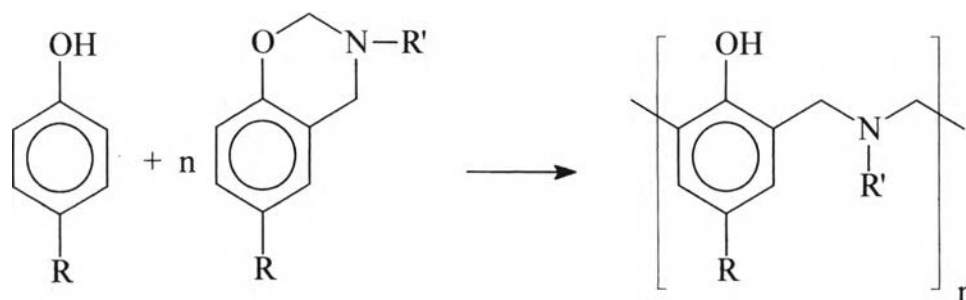


Figure 2.2 Ring-opening reaction of benzoxazine.

Ning and Ishida (1994) synthesized bifunctional benzoxazine based on bisphenol-A, formaldehyde and aniline which can be formed into crosslinked structure characteristics of phenolic materials through ring-opening reaction. The cured products exhibit excellent mechanical integrity and high glass transition temperature.

The curing behavior of the above benzoxazine precursor was studied by Ishida and Rodriguez (1995). They found that the curing behavior of as-synthesized benzoxazine precursor is autocatalytic and very similar to that of purified monomer. They also noticed that the presence of the phenol structure with free ortho position in as-synthesized precursor has a catalytic effect on the curing reaction.

Ishida and Allen (1996) reported that the ring-opening polymerization of benzoxazines occurs with either near-zero shrinkage or even a slight expansion upon cure. Moreover, they also studied the copolymers based on benzoxazine and epoxy (1996). The addition of epoxy to the polybenzoxazine network greatly increases the crosslink density of the thermosetting matrix and strongly influences its mechanical properties. The copolymerization reaction occurs via the opening of the epoxide ring by the phenolic hydroxyl functionalities present in the polybenzoxazine precursor, as shown in figure 2.3.

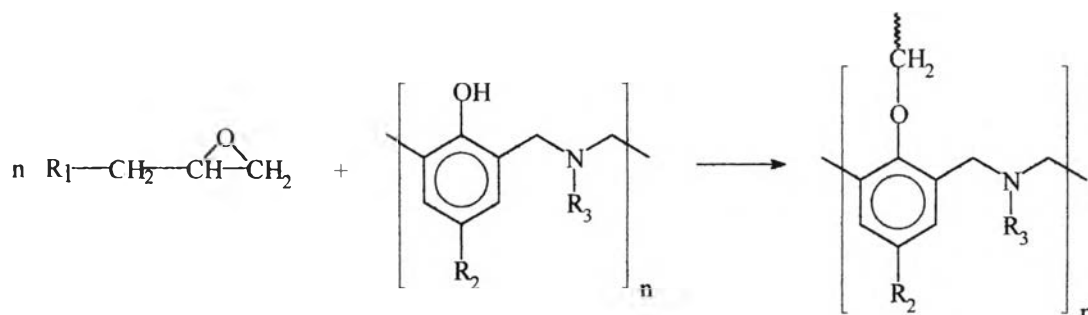


Figure 2.3 The copolymerization of the benzoxazine with an epoxy.

Ishida and Low (1997) reported that the volumetric expansion of the benzoxazine resin is mostly due to the consequence of molecular packing influenced by inter- and intramolecular hydrogen bonding.

The effect of CaCO_3 on the static and dynamic mechanical properties of polybenzoxazine based on bisphenol-A and aniline was studied by Suprapakorn, Dhumrongvaraporn and Ishida (1998). The tensile strength and flexural strength decreased while modulus increased with filler content.

The mechanical properties of the rubber-modified polybenzoxazine was reported by Jang and Seo (1998). Polybenzoxazine was modified with amine-terminated butadiene acrylonitrile rubber (ATBN) and with carboxyl-terminated butadiene acrylonitrile rubber (CTBN). They found that the stress intensity values, toughness and flexural strength of polybenzoxazine increased with the increase of rubber content while the flexural modulus decreased.

2.2 Spirosilicate Compounds

The widespread availability of silica and its low cost make it an ideal starting material for new routes to silicon feedstock chemicals. However, the major problem of using silica is its high silicon-oxygen bond energy. The silicon-oxygen bond cleavage during silica depolymerization by base catalyst is one way to solve this problem. The depolymerization of silica to

monomeric silicate compounds was first synthesized by Rosenheim *et al.* (1931). Silica was converted to hexacoordinated complexes in water by the reaction of silica with catechol and inorganic base, as shown in figure 2.4.

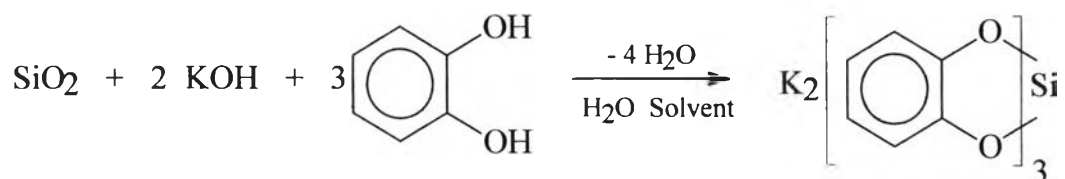


Figure 2.4 The depolymerization of silica to monomeric silicate compounds.

Allcock (1972) first synthesized neutral aromatic or tetracoordinated siloxanes, biscatecholsilane, by using carbothermally derived SiCl_4 . Later, Robinson (1990) synthesized bis(4-*t*-butylcatechol) silane, analogue of biscatecholsilane. The reactions of these materials are shown in figure 2.5.

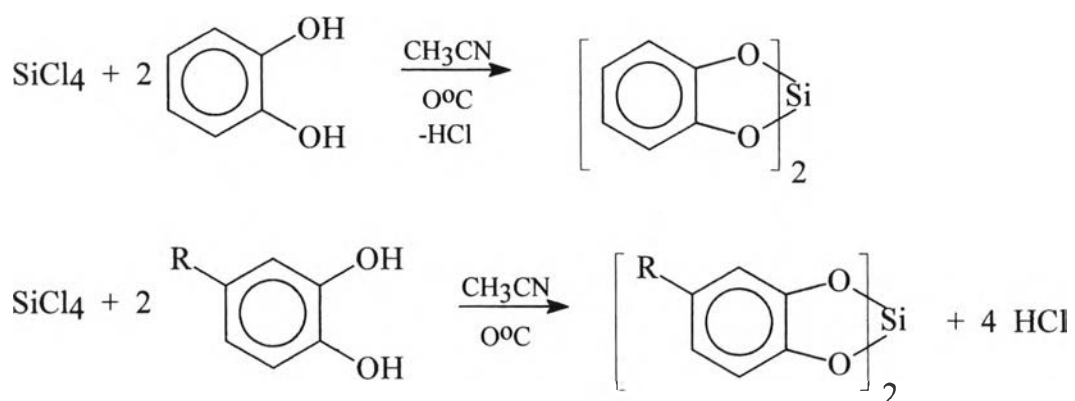


Figure 2.5 Synthesis of biscatecholsilane and bis (4-*t*-butylcatechol) silane.

Laine *et al.* (1994) synthesized pentacoordinated anionic and hexacoordinated dianionic glycolato silicate complexes by direct reaction of silica with equivalent amounts of group I/II metal hydroxides/oxide in excess ethylene glycol. The reactions are shown in figure 2.6.

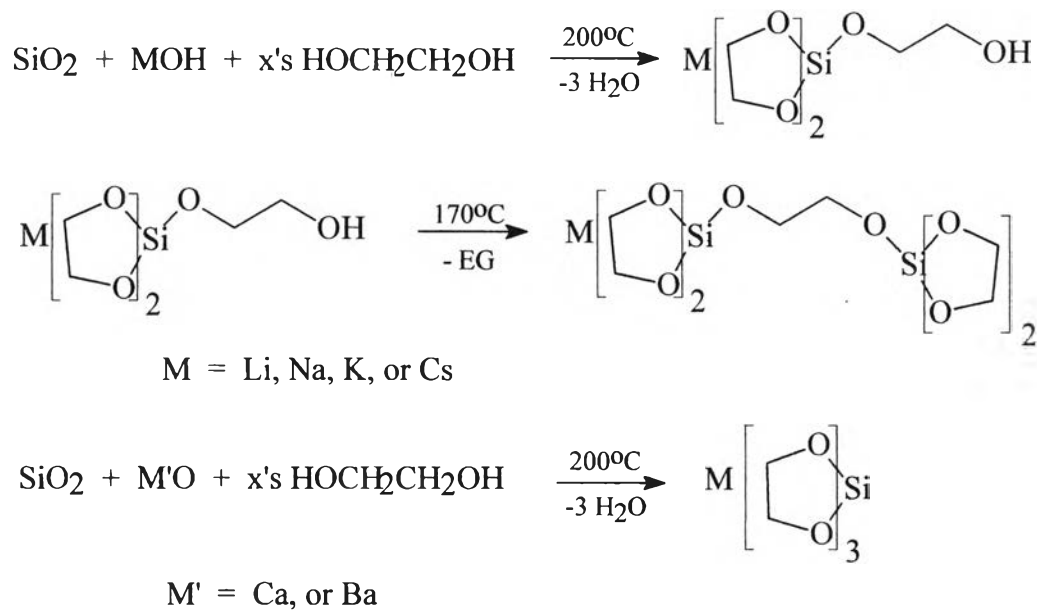


Figure 2.6 Pentacoordinated anionic and hexacoordinated dianionic glycolato silicate complexes.

Rangsitphol, Dhumrongvaraporn and Laine (1995) synthesized bis (1,2-dioxyphenyl) silane directly from silica and catechol using triethylenetetramine (TETA) as a catalyst. Later, Phongpisitsakun, Wongkasemjit and Laine (1997) synthesized the copolymer directly from silica, catechol and 4-*t*-catechol, as shown in figure 2.7.

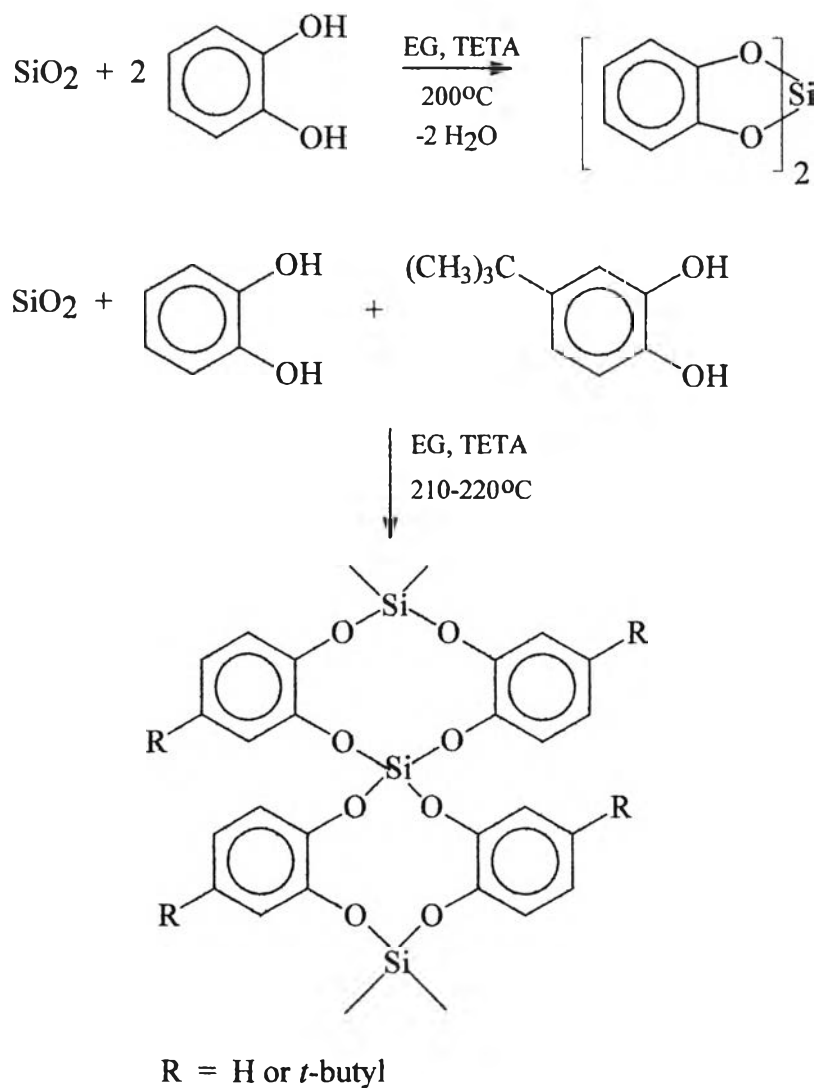


Figure 2.7 Bis(1,2-dioxyphenyl) silane and copolymer of catechol and *t*-butylcatechol.

Recently, spirosilicate compounds from silica and ethylene glycol/ethylene glycol derivatives were synthesized by Sun (2001). The reaction of spirosilicate compounds are shown in figure 2.8.

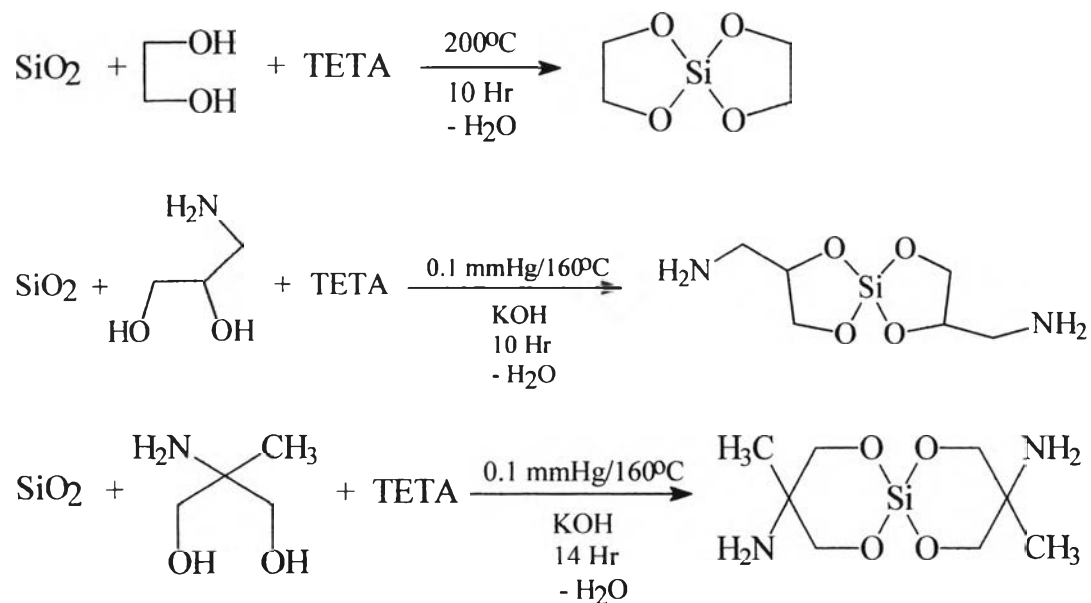
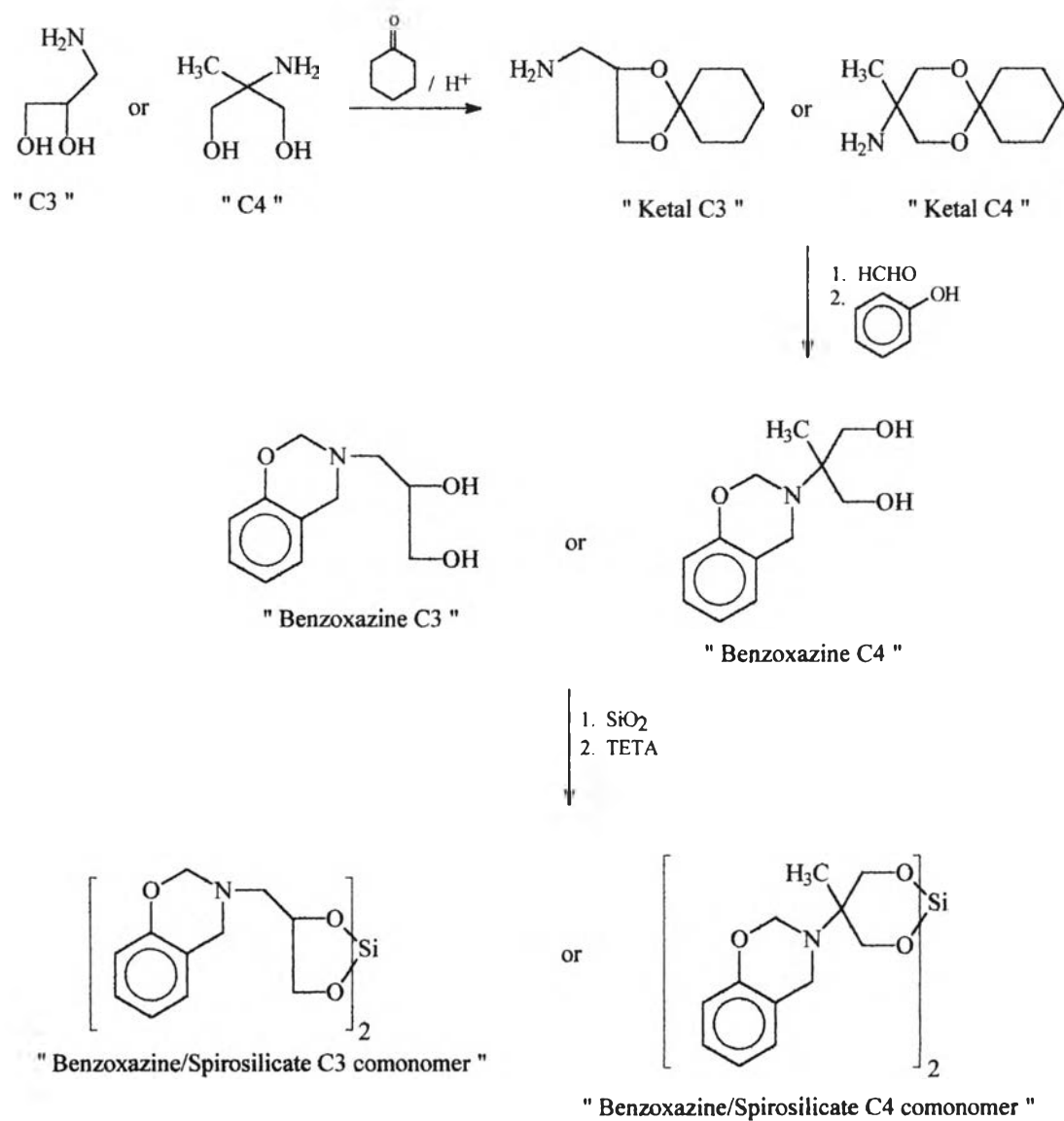


Figure 2.8 Synthesis of spirosilicate compounds.

The volumetric property of aminospirosilicate compounds was studied by Jitchum (2000). She found that the spirosilicates C3 and C4 show near zero shrinkage upon curing, 1.35% and 0.65%, respectively.

The aim of this research is to synthesize benzoxazine/spirosilicate copolymers via the following scheme.



Scheme 1 The reactions of benzoxazine/spirosilicate comonomers.