CHAPTER I
INTRODUCTION

Synthetic polymers are important in the modern life, especially phenolic resins which are the oldest synthetic polymers. Phenolic resins are produced by the reaction of phenol with aldehyde which are raw materials from petrochemical supply, quite versatile and inexpensive. In most applications, phenolics are combined with reinforcing fillers or fibers to give a function as the adherent or the critical binder of the composition. These phenolic resins bonded materials, i.e. particleboards, molding materials, fiber insulation products, foundry cores, grinding wheels, friction elements, represent the largest consumption. Phenolics can also be copolymerised with other condensation polymers having attractive features, such as high temperature resistance, infusibility and flame retardance. Their applications involve several fields, for example, aerospace, appliance, automotive, construction, clothing and also medical.

While phenolics have many advantages, they do have disadvantages. They release the volatiles, such as H_2O, CH_2O, and NH_3 during curing process, which makes fabrication of void free materials extremely difficult. Due to their brittleness, they are usually used with fillers. Phenolics can be cured with strong acids to produce novolac or bases to yield resole materials. These processes cause the corrosion effect. In addition, phenolic materials have poor molecular design flexibility since the main structures; phenol, and formaldehyde, cannot be changed much. Thus, if these problems can be overcome, it will be greatly useful in commercial applications, and benzoxazines based phenolic resins have been developed as a new alternative to overcome the shortcomings.

1.1 Benzoxazine

A phenolic derivative, a ring compound formed from a primary amine and formaldehyde via Mannich reaction, is termed benzoxazine. Benzoxazines based phenolic resins overcome those drawbacks of the traditional phenolics. They were found to react with the ortho position of a phenolic compound to form a dimer with methylene-amine-methylene bridge structure. The process has no volatiles during curing because it proceeds by ring opening polymerization. Due to the synthesis by Mannich condensation of a phenol, formaldehyde and an amine, they do have much more molecular design flexibility than novolac and resole materials. Based on the main chain structure and the properties, polyoxazines provide tremendous freedom in design which can modify products based on the structure-property relationships.

The formation of benzoxazine compounds proceeds according to the reaction in figure 1.1.

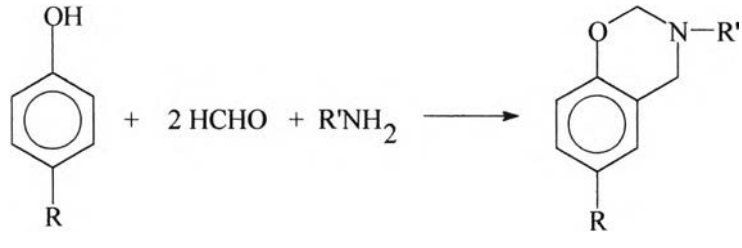

Figure 1.1 The formation of benzoxazine compounds.

The ring opening reaction of a monofunctional benzoxazine initiated by a para-substituted phenol is shown in figure 1.2.

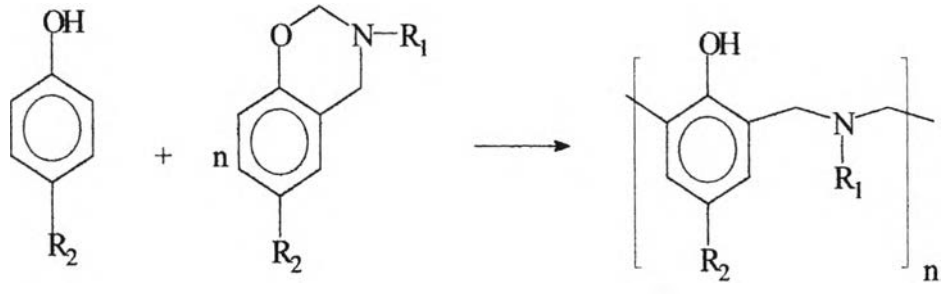

Figure 1.2 Ring opening reaction of a monofunctional benzoxazine initiated by a para-substituted phenol.

1.2 Spirosilicate Compounds

For phenolic resins, they require fillers, such as, cellulose flour, wood flour, and more commonly mineral fillers to reduce shrinkage, but these fillers can be abrasive to the mold surface. Various fillers are incorporated into the matrix and molding conditions are modified to reduce resin shrinkage. However, they can not delete this problem, only reduce it.

Bailey and co-worker (1973) introduced a series of spiroortho compounds which are spiroorthoesters and spiroorthocarbonates that expand upon curing.

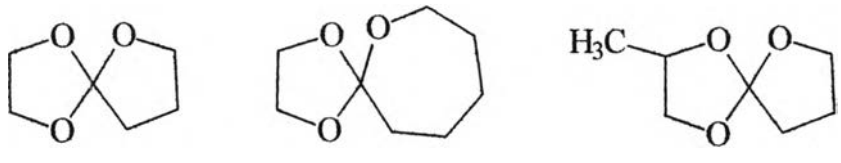

Figure 1.3 Examples of spiroorthoesters.

Sun (2001) successfully synthesized spirosilicate compounds directly from silica and ethylene glycol/ethylene glycol derivatives. Spirosilicate C3 is synthesized from silica and 3-amino-1,2-propanediol, while spirosilicate C4 is from silica with 2-amino-2-methyl-1,3-propanediol. Both are produced in the presence of TETA as both catalyst and solvent.

In the same year, Jitchum investigated the volumetric property of aminospirosilicate compounds. She found that the spirosilicates C3 and C4 show near zero shrinkage upon curing.