

## CHAPTER II

### LITERATURE SURVEY

Generally, thermosets pass one through a soft plastic state and harden irreversibly, and the first observed irreversible reactions required heat. Such plastics were called thermosetting. Polyesters are classified as thermosetting for general purpose and specialty resins. They account for the bulk of applications. Specialty resins are grouped into flame-resistant, light-stable, and weather- and chemical-resistant resins.

Like polyesters, epoxies are used for similar applications but are more expensive and manufacture is more complicated. Therefore, epoxies are used only if polyesters do not provide the desired properties.

The phenolic resins, which were developed in 1909, are the oldest thermosetting plastics and have a wide range of uses. They are produced mainly from phenols and aldehydes. The properties and manufacturing process of reinforced thermosetting plastics of these materials are shown in Table 2.1

In the case of phenolic resins, volatiles, such as, water or small molecules, are released due to the condensation reaction. These volatiles sometimes reduce the properties of cured phenolic resins because of the formation of a microvoid leading to the shrinkage in the materials. Another problems are listed as follows

- brittleness of the materials
- use of strong acids as catalyst
- poor shelf life
- toxicity of raw materials (especially phenol)
- high viscosity of the precursors

- a narrow processibility window

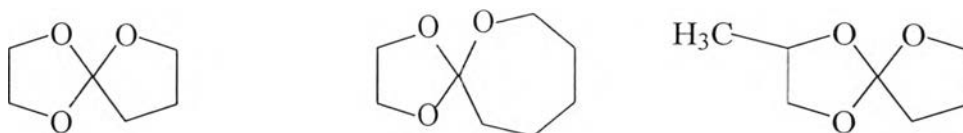
**Table 2.1** Properties and manufacturing processes of reinforced thermoset plastics.

Thermosets	Properties	Processes
Polyesters	Simplest, most versatile, economical, and most widely used family of resins; good electrical properties, good chemical resistance, especially to acids	Compression molding, filament winding, hand lay-up, mat molding, pressure bag molding, continuous pultrusion, injection molding, spray-up, centrifugal casting, cold molding, encapsulation
Epoxies	Excellent mechanical properties, dimensional stability, chemical resistance (especially to alkalis), low water absorption, self-extinguishing (when halogenated), low shrinkage, good abrasion resistance, excellent adhesion properties	Compression molding, filament winding, hand lay-up, continuous pultrusion, encapsulation, centrifugal casting
Phenolic resins	Good acid resistance, good electrical properties (except arc resistance), high heat resistance	Compression molding, continuous lamination

However, shrinkage in most thermosetting resins is quite high, 3-15 % and widely used epoxies undergo volumetric shrinkage of 2-7% upon curing. It causes residual stress, warping, premature debonding of the fiber from the matrix, fiber bulking, and delamination in fiber-reinforced

composites. In dental industry, methyl methacrylate end-capped diglycidyl ether of bisphenol-A has been used as the matrix for dental filling, the shrinkage upon curing has been a major problem of this resin in this field. In molding industry, shrinkage is the most important problem because of nonuniformity in the dimension of the molded parts. For phenolic resins, they require fillers, such as, cellulose flour, wood flour, and more commonly mineral fillers to reduce shrinkage (Knop, 1985) but these fillers can be abrasive to the mold surface. Various fillers are incorporated into the matrix and molding conditions are modified to reduce resins shrinkage but can not delete this problem, only reduce it.

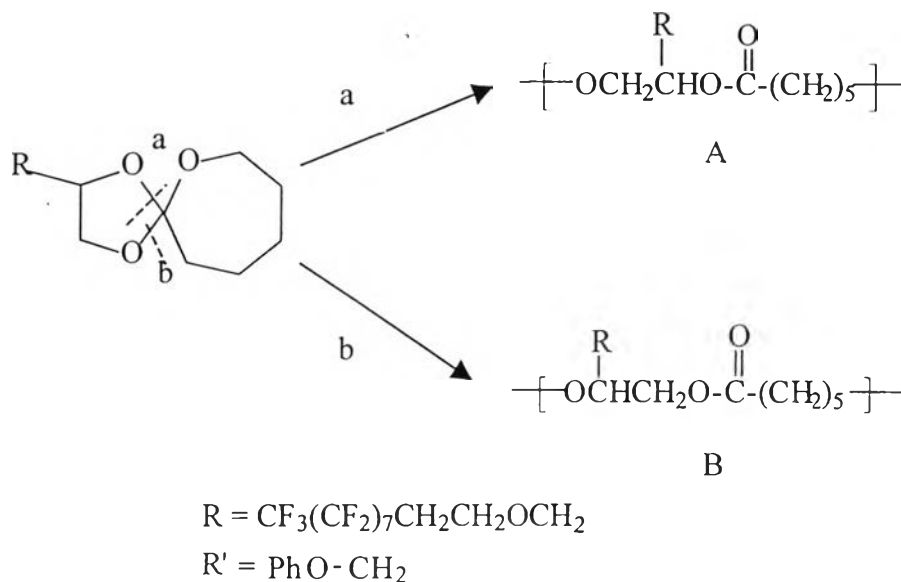
In the 1970s, Bailey and co-worker (1977) introduced a series of spiroortho compounds which are spiroorthoesters and spiroorthocarbonates that expand upon curing. Spiroorthoesters as well as bicyclic orthoesters often undergo cationic polymerization involving double ring-opening.



**Figure 2.1** Examples of spiroorthoesters.

Because of the chemical transformation of compact bicyclic monomer to linear polymer, most of these monomers show little or no volume shrinkage on polymerization. Spiroorthoester containing a perfluoroalkyl group underwent double ring-opening polymerization to give a poly(ether-ester) consisting of two kinds of structural units, which are formed by ring-opening at the O(4)-C(5) bond (part a) and the O(1)-C(5) bond (part b), respectively (Yokozawa, 1990) in Figure 2.2. The former unit A dominated

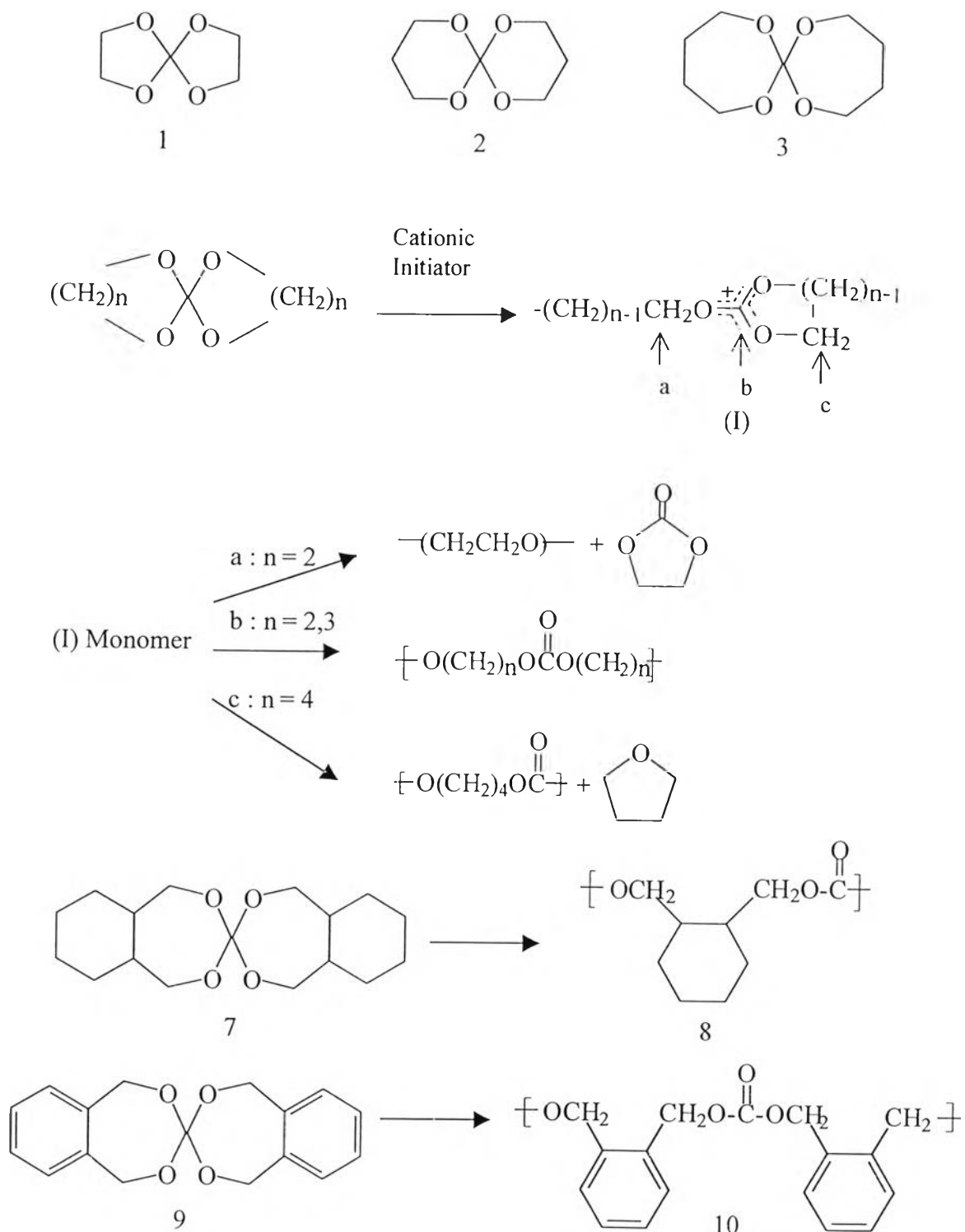
regardless of the polymerization temperature. Probably, the steric hindrance between the side chain of material and the propagating cation attacking the O(1) atom makes path b unfavourable.



**Figure 2.2** Polymerization of some spiroorthoesters.

Polymerization of spiroorthoesters which R is R', perfluoroalkyl group accompanied a 2.7% volume expansion. This behavior is similar to that observed in the polymerization of nonfluorinated spiroorthoester (R = R'), 0.9% expansion. Thus, it appears that the perfluoroalkyl group does not give significant effect on the feature of zero shrinkage during the polymerization of spiroorthoesters.

Sakai (1973) was the first to report the cationic ring-opening polymerization of three types of spiroorthocarbonates (1, 2 and 3) with boron trifluoride etherate as the initiator, as shown in scheme I. Concerning the three possible sites attacked by the monomer, irrespective solvent, initiator, and temperature, spiroortho compound 7 gave polycarbonate 8, whereas 9 gave poly(ether-carbonate) 10. The attack along the part b



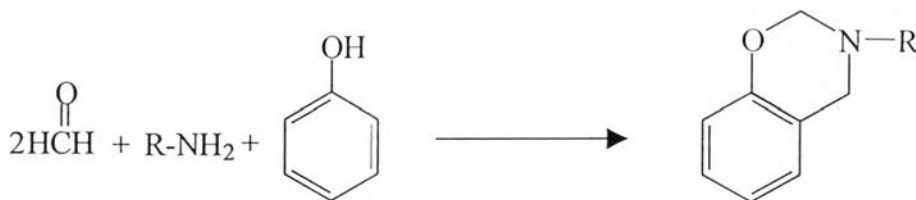
Scheme I

produces polymer 8, while the attack along part **c** gives polymer 10. This marked difference in polymerization behavior indicates that the propagating species of the benzo derivatives 9 is more reactive, i.e. more electrophilic, than that of 7.

Cationic polymerization of spiroorthocarbonates leading to a poly (ether-carbonate) alternating copolymer proceeds via the trialkoxycarbenium ion as a possible propagating species. Since this type of carbenium was found to be quite possible, the growing chain end was expected to remain living after the completion of the polymerization (Endo, 1990).

Many researcher groups have tried to introduce the spiroortho compound as an additive into epoxy resins to reduce shrinkage in the volume and improve the mechanical propertied. A copolymer of bisnorbornenyl spiroorthocarbonate and an epoxy were used by Lim and co-workers (Ishida, 1997). They found that the resulting composite had higher impact strength and higher shear strength than that of epoxy-carbon fiber composite. He and co-workers (Ishida, 1997) reported that 25% bisnorbornenyl spiroorthocarbonate content was found to be the suitable value for the mixture to expand upon cure. Unfortunately, spiroortho compounds by themselves found a few useful applications. Other disadvantages include complicated synthesis procedures and low glass transition temperatures ( $T_g$ ); they have not thus been used as engineering polymers.

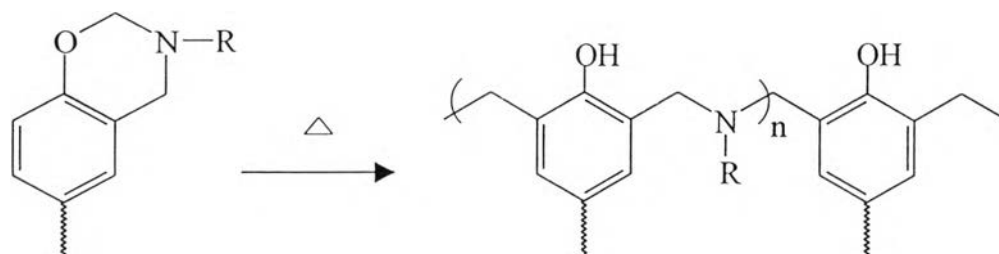
Benzoxazines, the novel phenolic resins which are the new materials that solve the problems related to traditional phenolic resins, were first synthesized by Holly and Cope (1944) from aldehyde, phenol derivatives and primary amine that shown in scheme II.



Scheme II

Monofunctional heterocyclic compounds of benzoxazine resins were studied by Riess (1986). They found that only oligomeric phenolic structures could be obtained because the thermodissociation of the monomer was always competing with the chain propagation. Ning and Ishida (1994) synthesized bifunctional benzoxazine precursors to overcome the low degree of cure of the compounds prepared by Riess (1986).

It is well known that the benzoxazine ring is heterocyclic structure consisting of a benzene ring fused with an oxazine ring, a six-membered ring that includes one oxygen and one nitrogen atom. This ring is stable at low temperature, but the ring-opening reaction occurs at high temperature, and novolac type oligomer having both the phenolic hydroxyl group and the tertiary amine group are produced, as shown in scheme III.



Scheme III

The properties of benzoxazines are typical for phenolic resins. They exhibit good heat resistance, flame retardance and have good dielectric properties in addition to excellent glass transition temperatures ( $T_g$ ), moduli, low water absorption values and near zero shrinkage property (Ishida, 1997) due to the consequence of molecular packing influenced by inter- and intramolecular hydrogen bonding. Some benzoxazines have been found to display interesting pharmaceutical properties including anti-inflammatory and central nervous system, depressing agents, an antibacterial activity against *Staphylococcus aureus* and *Escherichia coli* (Russell, 1998)