CHAPTER 2

THEORETICAL BACKGROUND

2.1 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is one of the powerful thermal characterization and most useful analytical techniques with minimal sample preparation.[2, 3] Quantitative information can be obtained from only a few milligrams of material. DSC measures the change in the heat capacity of a sample as a function of temperature by measuring the heat flow required for maintaining a zero temperature differential between sample and reference cells. DSC curves are plotted as a function of whether time or temperature at a constant heating rate. Figure 2.1 shows a typical curve obtained from polymeric sample. It provides relationships between thermal properties and molecular structure, processing, morphology, and other properties.

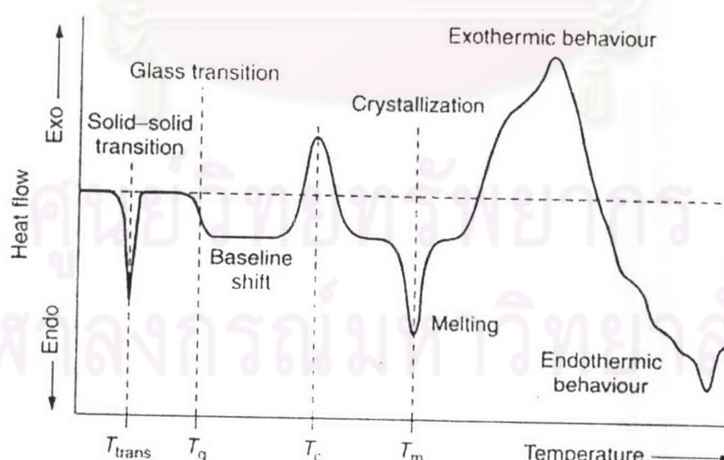

Figure 2.1 A typical DSC curve of a polymer.

By varying the heating rates, it is possible to investigate the kinetic determinacy and simulation of polymer process. Two approaches to determine kinetic parameters are isothermal (time scans) and non-isothermal (temperature

scans) methods. For thermosetting encapsulants, which require a rather high curing temperature, the kinetic parameters cannot be obtained accurately by the measurements operated under an isothermal condition due to instrumental and experimental factors. Non-isothermal analysis is generally preferred for the following reasons: (i) dynamic experiments are faster and the results are easier to interpret; (ii) the reaction process can be followed over a wide range of temperatures; (iii) several reaction steps can be observed in a single experiment; and (iv) a number of methods of data evaluation are available. Thus, in this study, the non-isothermal DSC was used to determine the kinetic parameters. By this technique, it is common to assume that the rate of evolution of exchanged heat is strictly proportional to the rate of the global chemical reactions at any instance, as followed:[3]

$$\frac{dH}{dt} = \Delta H_R \frac{d\alpha}{dt} \tag{2.1}$$

where $\left(\frac{dH}{dt}\right)$ is the heat generated in a unit time or heat flow (DSC ordinate), $\left(\frac{d\alpha}{dt}\right)$ is the reaction rate, and ΔH_R is the heat of reaction obtained from the area of the DSC thermogram.

Therefore, it is possible to evaluate the reaction rate $\left(\frac{d\alpha}{dt}\right)$ and the degree of conversion (α) reaching at time *t*, by the following expressions:[3]

$$\frac{d\alpha}{dt} = \frac{1}{H_R}\frac{dH}{dt} \qquad ;\alpha = \frac{\Delta H_t}{\Delta H_R} \tag{2.2}$$

where ΔH_t is the heat released up to time *t*, and it can be obtained by the integration of the calorimetric signal $\left(\frac{dH}{dt}\right)$ up to time *t*.

According to the chemical kinetics, the reaction is activated when a particle of the reactant attains sufficient energy to overcome the potential energy barrier impeding the reaction. The rate of reaction is given by: [3]

$$\frac{d\alpha}{dt} = kf(\alpha) \qquad (2.3)$$

where $f(\alpha)$ represents an empirical function of the conversion-dependent of rate equation; and k is the coefficient given by Arrhenius equation: [3]

$$k = A\exp\left(-\frac{E_a}{RT}\right) \qquad (2.4)$$

where A (s^{-1}) is the pre-exponential factor (so called the frequency factor); E_a ($kJmol^{-1}$) is the activation energy; T (K) is the temperature of the sample; and R ($Jmol^{-1}K^{-1}$) is the gas constant.

By combining equations 2.3 and 2.4, the following expression is obtained: [3]

$$\frac{d\alpha}{dt} = Af(\alpha)\exp\left(-\frac{E_a}{RT}\right) \qquad (2.5)$$

In its most commonly presumed form of solid-state reactions $f(\alpha) = (1-\alpha)^n$ where n is the reaction order. Equation 2.5 is generally written as: [3]

$$\frac{d\alpha}{dt} = A(1-\alpha)^n \exp\left(-\frac{E_a}{RT}\right) \qquad (2.6)$$

Two important methods (i.e., Kissinger's method and Ozawa's method) are commonly employed to calculate the activation energy without assuming any model and integrating the exothermic peak.

(i) In Kissinger's method[4], it is assumed that the maximum in the DSC thermatogram occurred at the temperature of the maximum reaction rate. A differentiation with time on the equation 2.6 was carried out. At the maximum rate, the term $\frac{d}{dt}\left(\frac{d\alpha}{dt}\right)$ is zero and gives the equation 2.7. [4]

$$\frac{\beta E_a}{RT_m^{\ 2}} = An\left(1-\alpha\right)_m^{\ n-1} \exp\left(-\frac{E_a}{RT_m}\right) \tag{2.7}$$

where β is the heating rate $\left(\frac{dT}{dt}\right)$ and T_m is the temperature at peak maximum.

By substituting an approximate solution to equation 2.6 into equation 2.7 and differentiating the obtained result, the following expression is obtained: [3]

$$\frac{d\left(\ln\frac{\beta}{T_m^{\ 2}}\right)}{d\left(\frac{1}{T}\right)} = \frac{-E_a}{R} \tag{2.8}$$

Equation 2.8 can be integrated and written as: [3]

$$-\ln\left(\frac{\beta}{T_m^{\ 2}}\right) = -\ln\left(\frac{AR}{E_a}\right) + \frac{E_a}{RT} \tag{2.9}$$

By this method, the plot of $\ln\left(\frac{\beta}{T_m^{\ 2}}\right)$ against $\frac{1}{T}$ gives a straight line with a slope of $-E_a$.

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(ii) Ozawa's method[5], at the constant heating rate, integration of equation 2.5 obtained: [5]

$$\int_{\alpha_0}^{\alpha} \frac{d\alpha}{f(\alpha)} = -\frac{A}{\beta} \int_{T_0}^{T} \exp\left(-\frac{E_a}{RT}\right) dT \quad (2.10)$$

where T_0 is the starting temperature.

This method assumes that the degree of conversion is constant for all heating rates. By substituting an approximate solution equation 2.6 into equation 2.10, the following expression is obtained: [5]

$$-\log \beta_1 - 0.4567\left(\frac{E_a}{RT}\right) = -\log \beta_2 - 0.4567\left(\frac{E_a}{RT}\right) = \ldots \quad (2.11)$$

A plot of ln β against $\frac{1}{T}$ gives a straight line of slope E_a.

To evaluate the reaction orders, the mechanistic models are assumed. There are two important models commonly used in a curing process of thermosets: (i) the nth order model including 1st and 2nd order kinetics, and (ii) an autocatalytic model. The mathematical expression of these two models can be written in the general terms as:[6]

n^{th} order kinetic model $\quad \frac{d\alpha}{dt} = k(1-\alpha)^n \quad (2.12)$

autocatalytic model $\quad \frac{d\alpha}{dt} = k(1+C\alpha^m)(B-\alpha)^n \quad (2.13)$

where m and n are reaction orders; B is the initial ratio between functional groups of resin and curing agent; and C is a relative weighting for autocatalytic part of the cure reaction.

2.2 Fourier Transform Infrared (FT-IR) Spectroscopy

Infrared spectroscopy is the study of interactions of infrared light with a matter.[7-10] It provides the specific information of molecular vibrations. When infrared light interacts with a matter, it can be absorbed and causing the vibrations of chemical bonds consisted in the material. There are two kinds of fundamental vibrations for a molecule: stretching and bending. Stretching is the movement along the bond axis (i.e., symmetric and antisymmetric) types. In the contrary, bending vibrations arise from changes in bond angle between two atoms and movement of an atomic group. It relates to the remainder of the molecule. As a result, molecule absorbs a certain energy that is quantized to raise the vibrational energy level and additionally exchange its electronic dipole moment. These cause absorption peaks appearing on an infrared spectrum at the wavenumber of light absorbed. Various stretching and bending vibrations occur at specific frequencies. Bending vibrations normally require less energy and occur at longer wavelength than those with stretching vibrations. Vibrational frequencies depend not only on the structures of specific atomic groups. But they are also affected to either greater or lesser degree by structures of the other parts of the molecule. Therefore, different molecules represent different vibration patterns due to different compositions in molecular structure. There is a correlation between the wavenumbers at which a molecule absorbs infrared radiation and its chemical structure.

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Since molecular vibrations readily reflect chemical feature of a molecule, such as an arrangement of nuclei and chemical bonds within the molecule, infrared spectroscopy contributes considerably not only to molecular identification but also studies of the molecular structure. Furthermore an interaction with the surrounding environment causes changes in molecular vibrations. As a consequence, infrared spectroscopy has become a useful technique for study of molecular interactions. The infrared spectrum can be divided into three categories: i.e., the far-infrared (< 400 cm^{-1}), the mid-infrared (400-4000 cm^{-1}), and the near-infrared (4000-13000 cm^{-1}) regions. Most infrared applications employ the mid-infrared region due to it contains fundamental mode of vibration of molecules. It is used to establish the identity of a

compound. However the near- and far-infrared regions can also provide specific information about materials. The near-infrared region consists mostly of overtone or combination bands of fundamental modes appearing in the mid-infrared region. The far-infrared region can provide such information regarding lattice vibrations.

An instrument utilized to obtain an infrared spectrum is called an infrared (IR) spectrometer. There are several types of IR spectrometers designed for spectral collection in the mid-infrared region. The most prevalent type is the Fourier transform infrared (FT-IR) spectrometer. FT-IR technique requires a substantially shorter operation time. It allows all resolution elements to be detected simultaneously throughout the spectral range whereas a dispersive-type instrument receives a signal only from one resolution element at a time. In addition FT-IR spectrometer has a higher signal-to-noise (S/N) ratio. As a result, it exhibits a greater sensitivity and good reproducibility for any system. The spectrum can be calculated and saved in the computer, thus FT-IR spectrometers have become a widespread technique for routine analysis.

According to basic of FT-IR spectroscopy, the Michelson interferometer is utilized instead of prisms and slits consisted in dispersive infrared spectrometers. Beamsplitter separates an incident beam into two paths and then recombines them again. Thus, the intensity variations of the exit beam can be measured by a detector as a function of travel path differences. The signal produced as a function of changes between the two beams. Figure 2.2 shows the schematic diagram of a Michelson interferometer.

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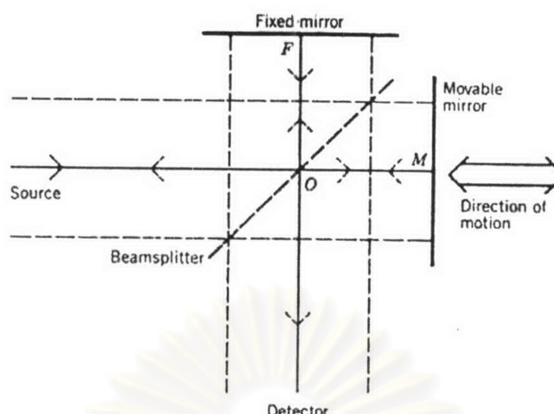

Figure 2.2 Schematic diagram of Michelson interferometer.

FT-IR spectrometer is based on the interference of light between two beams, producing an interferogram. Time and frequency domains are interconvertible by the Fourier transform method. The basic components of FT-IR spectrometer are shown schematically in figure 2.3. The radiation generated by the IR source passes through an interferometer, then being absorbed by a sample before reaching a detector. Upon the signal amplification, in which high-frequency contributions have been eliminated by a filter, the data are converted into a digital from by an analog-to-digital converter. Then they are transferred to the computer for of Fourier transformation. The finally FT-IR spectrum is obtained from the ratio of a single beam of the sample against that of the reference.

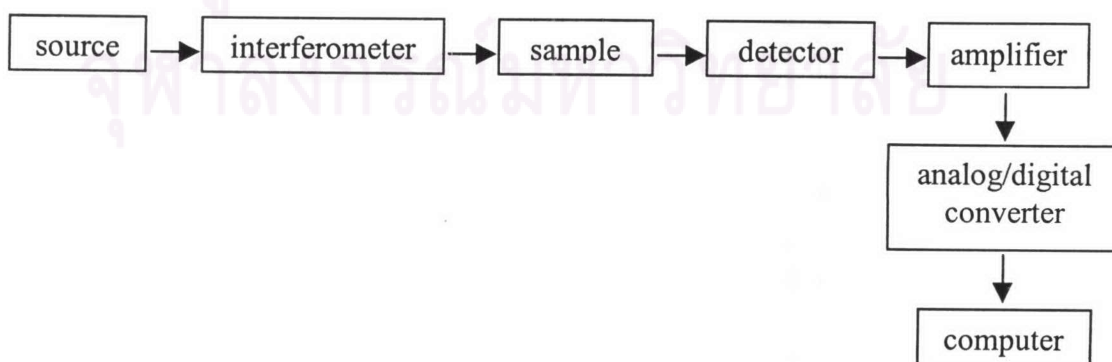

Figure 2.3 Schematic of a typical FT-IR converter spectrometer.

Polymer chains are made up of sequences of chemical repeating units. Since the stretching and bending vibrations in a polymer closely resemble to those in monomers, peak assignment of conventional infrared spectrum is practically applicable to polymer structure. It can be used to investigate many parameters such as polymer end group, chain branching, configuration, and conformation. It has also been used to identify and determine the concentration of impurities, antioxidants, emulsifiers, additives, plasticizers, fillers, and residual monomers in polymer materials. In addition, FT-IR spectroscopy is now widely employed to characterize curing process of thermosetting resins. In theory, the principle of kinetic building consists in the following evolution of a reactive vibration band of the resin versus curing treatments, time and temperature. To obtain the information on the kinetics of a reaction, the rate of appearance or disappearance of an absorption band is followed and the rate constant is calculated directly from the observed spectra. Changes in a number of reactive molecules can be investigated directly by absorption intensity (A) of characteristic vibration bands associated to a particular function group in the spectrum. Thus consumption of starting molecules and appearance of products can be determined from the Beer-Lambert law as:[9]

$$A = \log\frac{I_o}{I} = \varepsilon cl \tag{2.14}$$

where I_o is the intensity of the incident infrared beam (background spectrum); I is the intensity of the infrared beam following absorption (sample spectrum); ε is the absorption coefficient (absorptivity); c is the concentration of samples; and l is the pathlength of sample through which the infrared beam passes through.

The absorbance is measured in terms of peak height or peak area from FT-IR spectrum. The absorptivity is the proportional constant between concentration and absorbance. The absorptivity is an absolute measurement of infrared absorption intensity for a certain molecule at a specific wavenumber. It is a fundamental physical property of the molecule. Absorbance is a unitless quantity, so the unit of absorptivity is defined in *(concentration x pathlength)*$^{-1}$ to cancle the units of the

other two variables in Beer-Lambert 's law. As a consequence, the absorbance is linearly proportional to the concentration of sample.

In principle, transmittance (T) is defined as:[9]

$$T = \frac{I}{I_0} \tag{2.15}$$

By substituting equation 2.15 into equation 2.14 and by raising both sides of the equation to the power of 10 gives:[9]

$$10^{\varepsilon cl} = \frac{1}{T} \tag{2.16}$$

and by rearranging the above equation the following expression is obtained:[9]

$$T = 10^{-\varepsilon cl} \tag{2.17}$$

The above expression indicates that the transmittance is not linearly proportional to the concentration.

An infrared spectrum can be a plot of either absorbance or transmittance versus wavelength or wavenumber. Traditionally, infrared spectra have been plotted in the absorbance unit because it is linearly proportional to concentration.

2.3 Electronic Packages

Computers have two main components: (i) integrated circuit logic and chips, and (ii) the electronic package.[10, 11] Electronic packaging is referred to the housing and interconnection of integrated circuits (i.e., chip or die) to form an electronic system. The major functions of electronic packaging are provided adequate heat dissipation, power distribution, circuit support, and circuit protection. Since the

invention of silicon integrated circuit in 1958, the development in the area of electronic equipment is accelerated rapidly. Advance multi-media products, which commonly have a compact and intelligent concept, are now becoming more familiar in our daily lifes. Even the most efficient and reliable designed of integrated circuit design tend to be poor if its package is improperly design. Service conditions necessitating protection include moisture, heat, salt spray, oxygen, radiation, microorganisms, chemicals, and solvents. In addition, fragile microelectronic assemblies need coatings for protection against abrasion, handling, shock, and vibration. Electronic package has a dominant effect on electronic system cost, performance, weight, size, and long term reliability.

Electronic packages can be classified into three classes according to their sources i.e., (i) plastics, (ii) ceramics, and (iii) metals.

Metals are one of the earliest electronic packaging i.e., a metal transistor outline (TO). But now they are used only in a special case, which involved electromagnetic shielding. They are found in computer, medical and communication applications of high performance integrated circuits.

Ceramics are used for high-end electronic devices which reliability and hermeticity are important. They are found in military, aerospace, high performance computer, and communication industries. According to their hermeticity and heat dissipation capability, they are expensive, rather heavy, high in dielectric constant, fragile, and high firing temperature.

Plastics are widely used in the manufacture of electronic devices because of their low cost but high production capability. Because of their high processability and good reliability, a wide range of chemical and physical properties provided by molecular engineering makes polymers highly versatile in the electronic industry. High temperature polymers with a glass transition temperature (T_g) greater than 150^oC, are major materials utilized in the electronics industry. Traditional polymers used in electronic packages are polyurethanes, polyimides, epoxies, silicones, and

polystyrenes. The use of polymer in electronic industry can be classified into four categories: (i) thin films; (ii) protective gels; (iii) rigid bulk encapsulants; and (iv) printed circuit board materials. Typically, polyimides play a dominant role in thin film application, while silicones are selected almost exclusively for soft gel applications. Epoxies are used in the majority of encapsulant and print circuit board application.

Electronic package consists of a hierarchy of interconnections. They are divided into levels ranging from 0 to 4 as shown in figure 2.4. The zero level is the chip-level packaging. The first level is either single- or multi-chip modules. The second level is a card or a printed circuit board. The third level is the motherboard. And the fourth level is a gate.

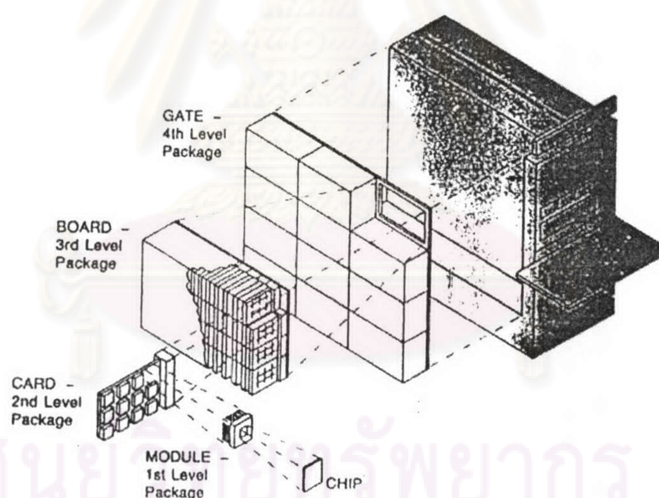

Figure 2.4 Schematic configuration of computer packaging hierarchy.

Encapsulants are the materials used to protect the chip from the environment, which can cause corrosion or degradation of chip materials. The materials must be resistant to radiation (ultraviolet, visible, and alpha particle), water diffusion, and mobile ions. They must also protect the devices from solvents, fluxes, cleaning agents, and fire. Figure 2.5 shows the cross-section of a typical plastic-encapsulated single-chip package.

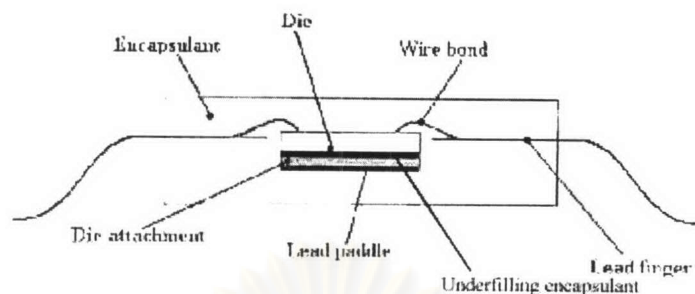

Figure 2.5 Cross-section of a typical first level package.

Some types of encapsulants i.e., underfilling are also used to mechanically couple the chip and the substrate. As a consequent they must have excellent mechanical and good dielectric properties. Because the integrated circuit is made from silicon, so encapsulants function as decreasing the residual stress in the solder joint caused by thermal expansion mismatch between the die and the substrate. Due to their low dielectric constants, encapsulants can reduce the device propagation delay. They must also be high purity since the impurity in an encapsulant can cause appreciable alpha particle radiation. The alpha radiation can generate a temporary "soft error" in operating dynamic random access memory (DRAM) services. This type of alpha particle radiation has become a major concern, especially in high-density memory devices. In addition, materials should possess low viscosities for voidless and short time encapsulation because the low viscosities are to ensure minimum void trapping in the materials. Voids act as the weak points, which will be subjected to thermal fatigue, thus affecting the performance and lifetime of the packaging materials. Low viscosity polymers are crucial for this type of application to ensure minimal void trapping in the fabrication process.

Plastic encapsulated devices were first introduced in 1960s. There are numerous polymeric materials that are used as electronic encapsulants. They are typically divided into three categories: (i) non-elastomeric thermoplastics; (ii) non-elastomeric thermosetting polymers; and (iii) elastomers. Thermoplastic polymers are materials that will flow when subjected to heat and will solidify upon cooling

without crosslinking. The examples of these types of encapsulants are polyvinyl chloride, polystyrene, polyethylene, and fluorocarbon polymers. Themosetting materials are crosslinking polymers that cannot be reversed to the original prepolymer after curing. Silicones, polyimides, epoxies, silicone-modified polyimides, polyesters, butadiene-styrenes, benzocyclobutenes, alkyd resins, allyl esters, and silicone-epoxies are examples of electronic thermosetting encapsulants. Elastomers are thermosetting materials of high elongation or elasticity. These types of materials consist of a long linear flexible molecular chain that is joined by chemical crosslinking. Silicone rubbers, silicone gels, natural rubbers, and polyurethanes are examples.

2.4 Benzoxazine Resin

The chemistry of benzoxazines dated back to the early 1940s. The benzoxazine moiety is a bicyclic heterocylcle. It is a single benzene ring fuse to another six-membered heterocyclic ring, containing one oxygen atom and a single nitrogen atom. It is produced by the Mannich-like condensation of phenol, formaldehyde, and amine. Benzoxazine is a useful intermediate for the conventional synthesis of some classical polymers. The synthetic reaction of benzoxazine is shown in figure 2.6. Various combinations of phenols and amines have been used to synthesize benzoxazine. Benzoxazine ring is stable at low temperature. However the ring-opening reaction can occur at high temperature. It produces the phenolic hydroxyl group and tertiary amine group. Traditional phenolic materials contain methylene bridges that link the phenolic group whereas polybenzoxazine contains carbon-nitrogen-carbon (Mannich base) bridge linking the phenolic moiety together.[12]

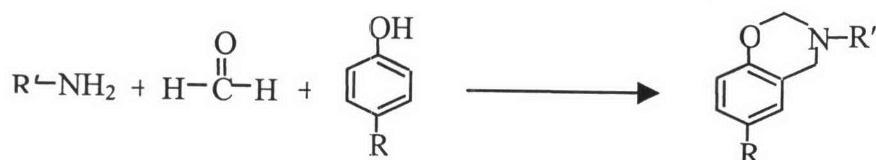

Figure 2.6 The synthetic reaction of benzoxazine.

In principle, the ring-opening reaction and the Mannich-bridge formation are consecutive reactions, whereby the trisubstituted benzene rings are consumed immediately after opening the oxazine ring. This correspondence continues throughout the curing process. Ring-opening reaction of benzoxazine is shown in figure 2.7.[13]

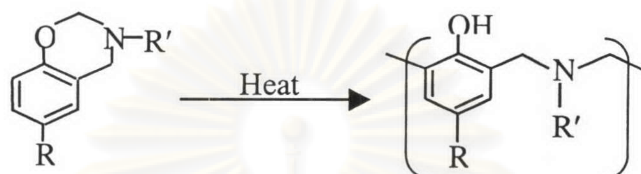

Figure 2.7 Ring-opening reaction of benzoxazine.

Upon heating the opening of oxazine ring and polymerization of monomers into oligomers and polymers can be investigated by the change in the 1500-800 cm^{-1} spectral region. The benzene rings from the backbone of a monomeric benzoxazine molecule are tri-substituted. During polymerization, the oxazine rings open and propagate while the benzene ring backbone becomes tetra-substituted.

Polybenzoxazine is a novel class of a thermally stable polymer. It is a specific class of a phenolic polymer. Polybenzoxazine has excellent properties commonly found in the traditional phenolics such as heat resistance, good electrical properties and flame retardance. It does not release by-products during polymerization due to ring-opening mode of polymerization. It also has unique properties, unlike traditional phenolics such as excellent dimensional stability, improved toughness, stable dielectric constant, near zero shrinkage, and low water absorption. In addition, polybenzoxazine can be cured without a strong acid or a basic catalyst. Thus polybenzoxazine combines the thermal properties and flame retardance of phenolics with the mechanical performance and design flexibility of advanced epoxy resins. It has a potential use in many applications such as electronics, adhesives, and coatings.

2.5 Literature Survey

Benzoxazine was first synthesized by Holly and Cope[12] from phenolic derivatives, primary amine and formaldehyde. Bruke *et al.*[14, 15] found that benzoxazine rings react preferentially with the ortho positions of the free phenolic compounds to form a dimer with a Mannich bridge structure. However the use of benzoxazine as precusor to phenolic resin did not start until 1973 when Schreiber[16, 17] reported the formation of oligomeric phenolic compounds made from benzoxazines. Riess *et al.*[18] studied the synthesis and reaction of monofunctional benzoxazine compounds. They reported that only oligomeric phenolic structure could be produced due to the competitive chain propagation reaction. Ring-opening reaction of benzoxazine with phenolic hydroxy group is shown in figure 2.8. [18]

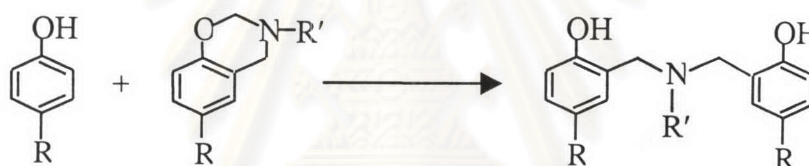

Figure 2.8 Ring-opening reaction of benzoxazine ring with phenolic hydroxyl group.

Ning and Ishida[13] synthesized the bifunctional benzoxazine precursors to yield high molecular weight polymers. The physical and mechanical properties of polybenzoxazines had been reported.[19] Ishida and Rodriguez[20] studied the polymerization kinetics of benzoxazine precursors by DSC. They found that the curing behavior of as-synthesized benzoxazine precursor is autocatalytic in nature and is very similar to that of a purified monomer.

Ishida and Allen[21] found that the ring-opening polymerization of benzoxazines occurs with near-zero shrinkage or even a slight expansion upon curing. In addition, they also reported that the copolymerization of benzoxazine with epoxy yields copolymer that had both a higher crosslinked density and glass transition temperature than those of polybenzoxazine homopolymer.[22] The copolymerization reaction occurs via the opening of epoxide ring by the

functionalities of phenolic hydroxyl presented in the polybenzoxazine precursor, as shown in figure 2.9. Kimura *et al.*[23] studied the curing behavior of these similar systems and the properties of the cured resins. Moreover, they also studied the copolymers based on benzoxazine compounds and epoxy resin or bisoxazoline.[24,25] It was reported that the cured resins from benzoxazine compounds and epoxy resin or bisoxazoline had superior heat resistance, electrical insulation, and water resistance as compare to those with the cured resins produced from traditional bisphenol-A type novolac and epoxy resin or bisoxazoline.[23]

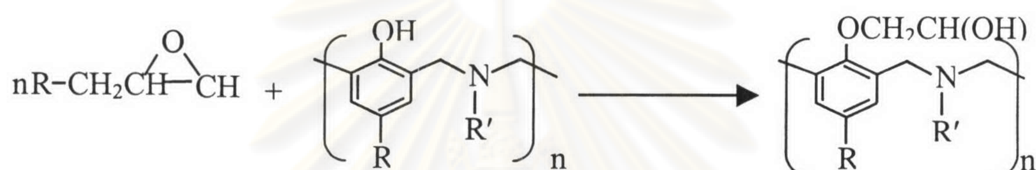

Figure 2.9 Copolymerization of benzoxazine with epoxy.

Ishida and Low[26] investigated the effect of intramolecular hydrogen bonding on volumetric expansion of benzoxazines by systematically varying the types of the primary amines used in the synthesis. Intramolecular hydrogen bonding occurs in these materials between the phenolic OH and nitrogen of the Mannich base. The strength of this hydrogen bonding depends on the electronegativity of the amine group attached to the nitrogen. The stronger the hydrogen bonding, the greater the volumetric expansion. In addition the steric effect of the amine group also influences the volumetric change during a curing process. Supa *et al.*[27] studied the temperature dependency of various hydrogen bonding in the phenolic novolac and polybenzoxazine resin. They found that the intermolecular hydrogen bonding is more sensitive to temperature than the intramolecular hydrogen bond.

Rimdusit and Ishida[1,28] synthesized the ternary systems based on benzoxazine, epoxy, and phenolic resins. The materials showed a wide range of desirable reliability and processability, which are highly dependent on the composition of the monomers in the ternary mixture. Intriguing physical, mechanical, and rheological properties of these systems had been reported.[29,30]

Ishida and Lee[31,32] studied the polybenzoxazine and polycarbonate blends. They found that the ring-opening polymerizations of benzoxazine were inhibited by the polycarbonate. The trans-esterification between the hydroxyl groups of polybenzoxazine and the carbonate groups of polycarbonate can be occurred. In addition, they also studied the polybenzoxazine and poly(ε-caprolactone) blends.[33,34] They reported that the blends show improved mechanical and thermal properties compare to polybenzoxazine homopolymer.

Wang and Ishida[35,36] studied the effect of various initiators on the benzoxazine polymerization. They found that the ring-opening polymerization of the benzoxazine family follows a cationic polymerization.