การสลายด้วยความร้อนของวัสดุห่อหุ้มชิ้นส่วนอิเล็กทรอนิกส์ชนิดใหม่ที่ได้จากระบบเทอร์นารีของเบนซอกซาซีน เอพอกซี และฟีนอลิกเรซิน

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THERMAL DEGRADATION OF A NEW ELECTRONIC PACKAGING MATERIALS BASED ON TERNARY SYSTEMS OF BENZOXAZINE, EPOXY, AND PHENOLIC RESINS

Miss Nopparat Thaweewathananon

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ได้สังเคราะห์วัสดุห่อหุ้มชิ้นส่วนอิเล็กทรอนิกส์ชนิดใหม่จากระบบเทอร์นารีของเบนซอกซาซีน เอพอกซี และฟีนอลิกเรซิน ซึ่งมีสมบัติเด่นที่หลากหลายขึ้นกับสัดส่วนของเรซินแต่ละชนิด ในการศึกษาการสลายตัวของพอลิเมอร์ที่เตรียมได้ โดยการวิเคราะห์ทางความร้อนด้วยเทอร์มอลกราวิเมทริก และฟูเรียร์ทรานส์ฟอร์มอินฟราเรดสเปกโทรสโกปีทำให้สามารถติดตามการเปลี่ยนแปลงโครงสร้างของเทอร์พอลิเมอร์ระบบเทอร์นารีนี้เนื่องจากความร้อนที่อุณหภูมิการสลายตัวต่างๆได้ และมีการเสนอกลไกการสลายด้วยความร้อนของเทอร์พอลิเมอร์ระบบเทอร์นารีโดยมุ่งไปที่การแตกพันธะของ Mannich base เป็นสำคัญ ซึ่งเป็นผลจากการสนับสนุนของการศึกษาการสลายด้วยความร้อนของพอลิเบนซอกซาซีน เอพอกซี ฟีนอลิก โคพอลิเมอร์ระหว่างเบนซอกซาซีน กับเอพอกซี และโคพอลิเมอร์ระหว่างเบนซอกซาซีน กับฟีนอลิกพบว่าเกิดการแตกพันธะที่ Mannich base ก่อน

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NOPPARAT THAWEEWATTHANANON: THERMAL DEGRADATION OF A NEW ELECTRONIC PACKAGING MATERIALS BASED ON TERNARY SYSTEMS OF BENZOXAZINE, EPOXY, AND PHENOLIC RESINS. THESIS ADVISOR: ASST. PROF. SANONG EKGASIT, Ph.D. THESIS CO-ADVISOR: SARAWUT RIMDUSIT, Ph.D. 75 pp. ISBN 974-17-1490-4.

A new electronic packaging material based on ternary system of benzoxazine, epoxy, and phenolic resins has been synthesized. Many properties of the resin can be altered by changing composition of the reacting components. In this study, thermal degradation of terpolymer has been investigated. Thermal gravimetric analysis (TGA) has been employed for determining thermal properties of the terpolymer while Fourier transform infrared (FT-IR) spectroscopy is utilized for observing of structural change during the degradation process. Mechanisms of thermal degradation have been proposed. It is also proposed that the Mannich base in the terpolymer plays an important role in the thermal degradation of the terpolymer. The proposed mechanism has also been supported through the thermal degradation study of polybenzoxazine, epoxy resin, phenolic resin, copolymer of benzoxazine and epoxy resin, and copolymer of benzoxazine and phenolic resin.

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LIST OF ABBREVIATIONS

TGA : Thermogravimetric analysis
FT-IR : Fourier Transform Infrared
T_g : Glass Transition Temperature

LIST OF SYMBOLS

A : Absorbance
I_o : Intensity of the incident beam
I : Intensity of the infrared beam
ε : Absorption Coefficient
c : Concentration
l : path length of sample
T : Transmittance

CHAPTER 1

INTRODUCTION

1.1 Electronic Packaging

Electronic packaging is the art and science of creating a physical electronic product-the art being the development of new and unique electronic products whose concepts are born through human activities and the science representing the sum of human knowledge in various engineering disciplines employed in the creative process. It combines the engineering and the manufacturing technologies required to convert an electrical circuit into a manufactured assembly. Electronic package is the electromechanical assembly resulting from electronic packaging design and manufacture. The level of electronic package may range from the integrated circuit package assembly to a printed wiring board assembly to a subsystem or system package assembly [1].

Electronic packages can be classified into three different categories according to types of materials (i.e., plastic, ceramics, and metals). Ceramics are used for high-end electronic devices where reliability and hermeticity are important requirements (i.e., those in aerospace applications, high performance computer and communication industries). Though these types of packages are outstanding in theirs hermeticity and heat dissipation capability, they are expensive, heavy, high dielectric constant, fragile, and high firing temperature. Metal packages are found in computer, medical, and communication application for high performance integrated circuits. These types of packages are expensive and heavy. Plastics packages are used when hermeticity is not required and they account for nearly 90% by volume of all packages because of their low cost and high processability with improved reliability. Epoxy, silicone, diallyl phthalates, polyimides, and some thermoplastic are used in various parts of electronic packages [1]. Recently, a new class of electronic packaging materials based on the ternary mixture of benzoxazine, epoxy, and phenolic novolac resins has been developed. The material properties show a wide range of desirable reliability and processability, which are highly dependent on the composition of monomers in the resin mixture [2]. Epoxy resin is a type of polyether as show in figure 1.1. The material has been widely used in electronic area in such application as printed-circuit broads, microelectronic porting and encapsulation. Advantages of epoxy resins are good heat resistance, excellent adhesion to a variety of substrates, outstanding corrosion protection, low moisture absorption, and good insulation. One disadvantage of epoxy resins is its rigidity due to high crosslink density.

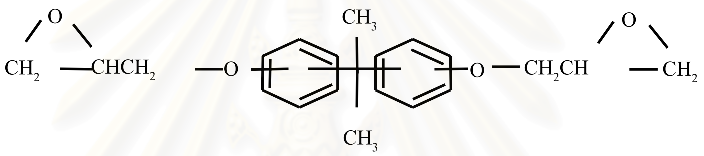


Figure 1.1 Epoxy resin (diglycidyl ether of bisphenol A epoxy resin (DGEBA)).

Phenolic novolac resin is a thermosetting polymer. It is synthesized from phenol and formaldehyde in acidic condition. Attractive features of phenolic novolac include low flammability and good heat resistance. However, drawbacks of phenolic novolac are its relatively high rigidity include rigidity and the production of by-product from its condensation reaction.

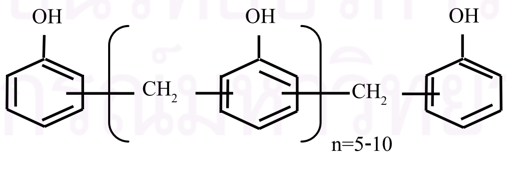


Figure 1.2 Phenolic novolac resin.

Polybenzoxazines are the same family as phenolic resin; however, polybenzoxazines have demonstrated advantages over conventional phenolic resin such as self-polymerization upon without releasing by-product, ease of processing from its low melt viscosity, high mechanical strength, high glass transition temperature, and high char yield.

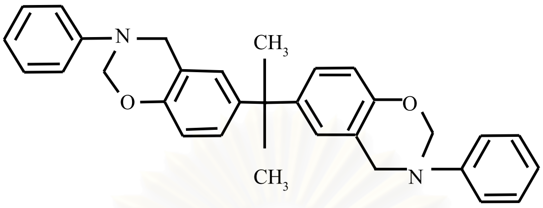


Figure 1.3 Benzoxazine resin (bisphenol A based benzoxazine, BA-a).

The ternary systems benzoxazine, epoxy, and phenolic resins show broad spectrum of useful properties depending on amount of reacting components. A glass transition temperature beyond 170^{o}C and thermal stability at 5% weight loss of 370^{o}C can be obtained from these systems. Phenolic novolac resin was reported to act mainly as an initiator for these ternary systems while low melt viscosity, flexibility, and improved crosslink density of the materials are attributed to the epoxy fraction. Polybenzoxazine imparts thermal curabality, mechanical properties as well as low water uptake to the ternary system. Thermal stability of electronic packaging materials is one major property requirement because electronic packaging materials are heated to elevated temperature upon working, sometime, up to relatively high temperature. Therefore, understanding thermal degradation of the material is necessary.

1.2 Thermal Degradation of Polymers

Thermal degradation is a cleavage process of polymer by heat whether at the service temperature or during polymer processing [3]. Various factors that affect the thermal degradation process are the environment of degradation, types of additives, and the structure of the polymer (i.e., molecular weight, degree of crosslinking, end group structure, and the structure of the substituents) [4].

The thermal stability of polymer is closely related to its bonding energies, e.g., polymer containing higher bonding energy result in more thermally stable materials [5]. For instance, fluorine-containing polymers tend to be one of the most thermally stable polymers and thus are able to be used at elevated temperatures. This results from the fact that the magnitude of C-F bond energy is greater than that of a C-H bond energy, which is in turn greater than that of a C-Cl bond energy. Phenomena: Effects of degradation on polymers may be assessed from the following:

- Changes in chemical structure. Oxidative degradation leading to weathering generally produces conjugated double bonds, carbonyl groups, and hydroxyl groups, which can be detected by IR spectroscopy.
- Loss in polymer mechanical properties.
- Embrittlement.
- Reduction in molecular weight due to chain scission or increase due to crosslinking.
- Generation of free radicals.
- Toxicity of products formed due to thermal degradation, pyrolysis, or combustion of polymers.
- Loss of additives and plasticizers.

1.2.1 Reaction Pathways to Thermal Degradation

When heated to the extent of bond rupture, polymers degrade by any of the following four routes:

1.2.1.1 Random Scission

This results from the production of free radicals along the backbone of the polymer (e.g., polyolefins), that causes the macromolecule to split into smaller molecules of varying chain lengths. When a free radical is formed along the length of polyethylene (PE), chain scission occurs, producing a molecule with an unsaturated end and another with a terminal free radical. This free radical may take hydrogen from an adjacent carbon, producing a saturated end with a new radical, or may combine with another free radical to form an alkane. Multiple cleavages produce molecules small enough to be volatile-with double bonds at both ends, one end, or neither.

1.2.1.2 Depolymerization

Depolymerization is a free-radical mechanism in which the polymer reverts to a monomer or monomers. When polymethyl methacrylate (PMMA) degrades by free radical depolymerization (unzipping), the molecule undergoes scission to produce an unsaturated small molecule (monomer) and another terminal free radical.

1.2.1.3 Side Group Elimination

Side group elimination is a two-stage process in which the polymer chain is first stripped of atoms or molecules attached to the backbone of the polymer, leaving an unsaturated chain (polymer). This polyene then undergoes further reactions, including scission, aromatization, and char formation. For example, Poly (vinyl chloride) or PVC first undergoes a loss of HCl to form conjugated polymer backbone. This unsaturated chain is further degraded to form aromatics and some smaller hydrocarbon chains. While this polymer and PMMA give close to quantitative yields of monomers during thermal degradation, other polymers such as polyethylene (PE) and polypropylene (PP) give negligible yields of monomers.

1.2.1.4 Cyclization and Carbonization

At 200-230^{o}C, polyacrylonitrile undergoes controlled thermal degradation to form thermally stable ladder polymers. At much higher temperatures, pyrolytic condensation and rearrangement of carbon network take place to form high-strength carbon fibers.

1.2.2 Analytical Techniques Applied in Thermal Degradation of Polymers

The thermal stability of a polymer can be evaluated by many thermal analyzers such as differential scanning colorimetry (DSC), thermogravimetric analysis (TGA), and thermal mechanical analysis (TMA) techniques, but these results can give only an estimate of stability and do not provide enough information to interpret the deterioration process itself. Several techniques, such as gas chromatography, radiochemical analysis, spectroscopic measurements [for example, NMR, Fourier transform infrared (FT-IR) spectroscopy, X-ray diffractrometry], or their combination have been developed and widely applied in the study of degradation mechanisms [6]. Those proposed from these results were based on degradation product analysis related to the original polymer structure. The degradation of material at high temperatures may cause rearrangement of the degradation fragments, secondary decomposition of primary products, or even more complicated reactions. Therefore product analysis only may lead to erroneous degradation mechanism. The combination of two useful techniques for this research i.e., FT-IR spectroscopy and TGA analysis may help elucidate the thermal degradation behaviors of our ternary systems and; hence, the possible way of further improving their thermal stability.

1.2.2.1 Thermogravimetric Analysis (TGA)

TGA is a thermal method that involves the measurement of weight loss as a function of temperature or time [5]. TGA can be used to quantify the mass change in polymer associated with transitions or degradation processes. TGA data provide characteristic curves for a given polymer because each polymer will show a unique pattern of reactions at specific temperatures.

1.2.2.2 Fourier Transform Infrared (FT-IR) Spectroscopy

Infrared spectroscopy can be used to investigate the effects of environmental exposure of polymers. Fourier transform infrared (FTIR) spectrometers can produce spectra of high accuracy in both intensity and frequency. FT-IR has been applied to the study of polymeric material, which include the oxidation and thermal degradation.

1.3 The Objective of This Research

Because electronic packaging materials are usually heated upon functioning, the understanding of thermal stability and decomposition of the materials is essential, especially for highly reliable systems. Therefore, an objective of this research is to investigate the thermal degradation processes of a new class of electronic packaging materials based on ternary systems of benzoxazine, epoxy, and phenolic resins by Fourier transform infrared (FT-IR) spectroscopy and thermogravimetry.

1.4 Scope of This Research

Understanding and monitoring a thermal degradation mechanism of thermal degradation of a new terpolymer based on ternary system of benzoxazine, epoxy, and phenolic resins for an application as electronic packaging materials.

CHAPTER 2

THEORETICAL BACKGROUND

2.1 Infrared (IR) Spectroscopy

Infrared (IR) spectroscopy is one of most often used spectroscopic techniques for polymer characterization. There are a number of reasons for the success of IR technique for material characterization. The method is practically rapid and sensitive with sampling techniques that are easy to use. In addition, the instrumentation is inexpensive compared to other spectroscopic techniques. Finally, interpreting the spectra is not difficult and can be learnt easily, although more in-depth better results may be obtained only by an infrared professional. In principle, IR spectroscopy is based on an absorption phenomenon and involves measuring the amount of energy that passes through or reflected from a sample and then comparing this amount to the light that transmitted or reflected from a perfect transmitter or reflector, respectively. An IR spectrum is a plot of the relative transmitted or reflected energy intensity as a function of frequency, normally in cm^{-1}.

2.1.1 Characteristic Group Frequencies in Vibrational Spectroscopy and Interpretation of Polymer Spectra Using Group Frequencies

Each polyatomic molecule is expected to have $3N$ vibrations (basically $3N$-6 when the three non-absorbing or zero energy translations and rotations of the molecule are counted) where N is the number of atoms in the molecule. These vibrational modes result in a unique spectral feature so called fingerprint, of the considered molecule. Careful cataloging of the IR spectra reveals an interesting correlation between the presence of certain chemical groups in the molecules and the corresponding IR absorption frequencies.

An infrared spectrum presents absorption bands in a narrow and predictable region as a result of specific chemical groups consisted in the molecule. This illustrates, as whenever a specific chemical group is presented, it would identify itself. Most IR spectroscopists have used these ‘characteristic group frequencies’ as structural probes for chemical groups in newly prepared molecules with unknown chemical structures. The spectrum is highly specific to the molecular framework of a molecule, as well as a high reproducibility representing for specific functional groups included in the molecular framework.

The vibrational modes of complex molecules fall quite naturally into two distinct categories: internal and external modes. As the name implied, the internal modes involve predominantly only a few selected atoms, and the external modes are principally related to the motions of all the atoms consisted in the entire molecule. The internal motions, such as stretching of chemical bonds or bending of bond angles in triatomic groups, are relatively unaffected by nature of the rest of the molecule and nearly have the same vibrational energy regardless of the molecular skeleton attached. When the internal modes are widely separated from each others and from the external modes, they have a characteristic group frequency that cannot be affected by the chemical nature or architecture of the rest of the molecule. In another word, these characteristic modes are uncoupled from the rest of the molecule and vibrate as if no other atoms were around. When a specific group is found in a number of different molecules, its uncoupled internal vibrations appear in the same narrow frequency region regardless of the type of molecular attachment. For example, a C-H bond appears between 3300 and 2700 cm^{-1} regardless of nature of the rest of the entire molecular structure. The particular type of C-H bond (i.e., aryl or alkane) results in a more specific absorption frequency within the same range. The concept of group frequency embraced by chemists generalized IR spectroscopy as a common qualitative technique. Catalogs of characteristic group frequencies have been reported in many literatures, and spectroscopists have tried to outdo each other with new and exciting structural assignments of group frequencies. The polymer chemists benefit as well because the characteristic group frequencies generally appear in the same region for polymers as for other chemical molecules. In some cases, specific couplings can occur with regularly ordered chemical functional groups in polymers. As a consequence, this condition shifts the group frequencies and therefore leads to valuable microstructural information of polymers.

The first approach to interpret an IR spectrum is to consider the resulted spectrum as a superposition of a number of group frequencies. Another is to confirm the existence of specific chemical groups by looking for other modes of this group (i.e., bending, twisting, and wagging modes) [8].

2.1.2 Fourier Transform Infrared (FT-IR) Spectroscopy

IR spectra were originally measured with a dispersive instrument equipped with an optical element of whether a prism or gratings in order to geometrically disperse the IR radiation. A scanning mechanism passes the dispersed radiation over a slit system to isolate the frequency range observed by a detector. In this manner, the spectrum (i.e., energy transmitted through a sample as a function of frequency) is obtained. This dispersive IR method is highly limited in sensitivity because a significant portion of the light does not fall onto the open slits and hence can hardly be detected efficiently. The sensitivity of the technique has then been improved with a multiplex optical device that allows all the transmitted energy to be observed simultaneously. The Michelson interferometer is such an optical device, and the IR instrumentation is consequently termed as Fourier transform infrared (FT-IR) spectrometer [7].

Multiplexing is the simultaneous encoding of a number of independent pieces of information in such a way that the information can be received by a single chanel system and later decoded into the independent contributing components [8]. A multiplex spectrometer is one that can achieve the spectral information of the molecule interested in terms of absorption intensity at individual frequency while measuring the intensities of all frequencies simultaneously with a single detector. In theory, sensitivity of the technique is improved with such a multiplex optical device (i.e., interferometers) due to the continuous detection of all transmitted frequencies simultaneously. The advantages of multiplexing include:

- Higher signal-to-noise ratio due to improved detector irradiance.
- Higher energy throughput because no slits are required.
- Higher accuracy in measuring the wavelength due to calibration with an internal laser.
- Higher speed of scanning achieved by interferometers than those with monochromators.
- Better signal-to-noise ratio as a result of signal averaging.

FT-IR spectroscopy combines the Michelson interferometer as multiplex optical device. In principle, the Michelson interferometer has two mutually perpendicular arms, as shown in Figure 2.1.

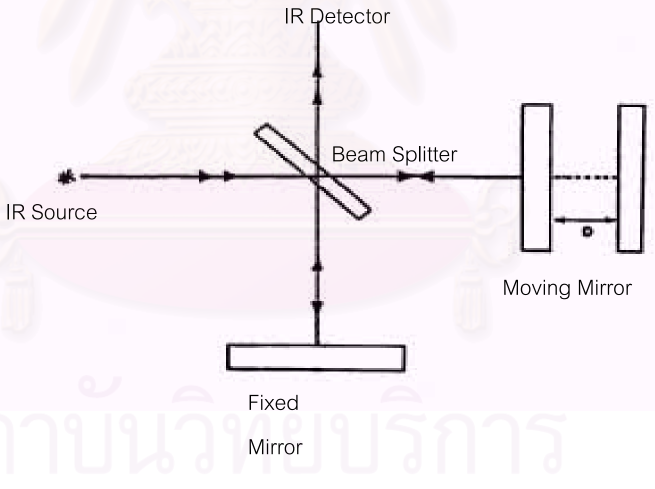


Figure 2.1 Schematic diagram of Michelson interferometer included in a Fourier transform spectrometer.

One arm of the interferometer contains a stationary plane mirror, whereas another arm is contained with a movable mirror. Bisecting the two arms is a beam splitter, constructed from an IR-transparent material, that divides the source beam into two equal beams traversing the two arms of the interferometer. These two light beams travel down their respective arms of the interferometer and then reflect back to beam splitter for recombination before going to the detector, as depicted. When the two mirrors are placed far away at equal distance from the beam splitter ($\Delta x = 0$, where Δx is the optical path difference), the beam path are identical. Under this certain condition, all wavelengths of radiation after recombination at the beam splitter produce a maximum flux onto the detector.

The moving mirror is generally driven on an air-bearing system. For FT-IR measurements, the mirror must be kept along the sample plane within 10 µm-rad for mirror driving up to 10 cm long. It is necessary to have some types of marker to initiate data acquisition at precisely the same mirror displacement every time. The uncertainty in mirror position cannot be greater than 0.1 µm from scan to scan. This precision is accomplished by a smaller reference interferometer. A visible white light source is passed through this reference interferometer, to produce a sharp centerburst or spike. Data acquisition is initiated when this centerburst reaches a predetermined value.

2.1.3 Transmission Spectroscopy

Transmission technique in IR spectroscopy has several advantages

- High signal-to-noise ratio when the sample has a proper thickness
- No sampling technique convolution of the spectra
- Easy quantification

Transmission spectroscopy is primarily useful for uniform (no holes, no variation in thickness) thin film of polymeric samples. For solid like polymers, a number of methods are available for making the sample sufficiently transparent for transmission measurements.

A thin film can be prepared by solvent casting. The method requires a solvent, which dissolves the sample, preferably at room temperature, and can be easily removed (i.e., having high vapor pressure) without formation of bubbles trapped in the sample film. Solvents such as chloroform (bp. 61.2^{o}C), acetone (bp.

56.2 ^{o}C), trichloroethanol (bp. 151 ^{o}C), *o*-dichlorobenzene (bp. 180.5 ^{o}C) and water (bp. 100 ^{o}C) can be used and selected depending on nature of the sample. Several drops of the solution are placed on an inert infrared-transmitting substrate (e.g., KBr or NaCl) and the solvent is then evaporated to leave the sample film on the substrate. If the film is too thin, an additional deposition onto the original dried film can be made to increase the film thickness. In some cases, the film can be peeled off the substrate as a freestanding film and placed in an IR holder for spectral collection. The limitations of the solvent casting technique are residual solvent interfering with the spectrum of the sample, and bubbles in the cast film, which produce a nonuniform film.

Thermoplastic polymers can be made as thin films by compression molding. This technique requires meltable samples and spacers for controlling the sample thickness of the sample itself. Teflon-coated aluminum (Al) foil is generally used over the press platens, so the film can be easily removed. The disadvantage of compression molding is loss of thermal history information of the sample.

In addition, powders or fluff of polymers can be studied with the transmission technique by forming a KBr pellet. This approach disperses the sample in an infrared transparent matrix (e.g., KBr or NaCl). These inorganic salts have the property of cold flow, so they would revert to a glass-like consistency when sufficient pressure (10-15000 lb/in^{2}) is applied to a finely devided powder. In this method, KBr is usually mixed with ~1% of finely ground sample in a special die. Pressure is applied by a press. The sample pellet formed is placed against the beam path inside a spectrometer to start data collection. Use of an alkali halide matrix to support a solid sample for IR analysis was first presented by Stimson in 1952. This technique has been employed widely because of its general applicability. The limitation of KBr method, in addition to the difficulty of making suitable pellets, is that some samples are polymorphic and would be converted when being ground with KBr at high pressure. However, it is very difficult to obtain uniform, transparent KBr pellets. Moisture in the KBr matrix is another problem because it makes pellets cloudy leading to high portion of scattering light. NaCl (cutoff 600 cm^{-1}), KBr (cutoff 400 cm^{-1}), and CeI (cutoff 200 cm^{-1}) have also been used.

Under a common experimental condition, preparation of clear neat powder pellet is difficult. An imperfect pellet results in light scattering and baseline shift. Improper sample dispersion can lead to improper absorbance measurements caused by the wedge shape of sample.

Powdered samples can be ground into a mull with Nujol (mineral oil), so that the particle size is normally smaller than the highest frequency of radiation used (typically 4000 cm^{-1}). Since Nujol has only a limited number of absorption bands, broad windows are available for analysis. However, grinding uniform, small particles in the mull is difficult. In case of hydrocarbon polymers that the C-H stretching of Nujol can interfere sample signal, it is possible to do Fluorolube mulling. The preparation process is the same as for Nujol but Fluorolube has no C-H stretching peaks, hence it can be used to obtain information in the 4000-1350 cm^{-1} spectral range.

Transmission spectroscopy is a traditional sampling method for qualitative analysis for purposes of polymer identification. Almost all of the IR spectral catalogs gathered in reference IR library is based on transmission measurements. For identification purpose of unknown samples, transmission technique has been become the primary sampling technique. On the other hand, transmission spectroscopy is useful for quantitative measurements only when uniform (no holes, no variation in thickness, no orientation) thin films of polymeric samples are available. The polymeric films should be sufficiently thin to allow observation of spectral absorbance values in the linear domain. In general, the absorbance value in the linear range is less than 1 for the major portions of the spectra, and particularly for those frequencies of which spectral subtractions are anticipated. This is needed for quantitative analysis of thin films. In polymer films practical, should be prepared in a thickness range of 10-100 μm. Solvent casting or compression molding method is usually required for film preparation. On the other hand, these techniques transform the sample by whether melting or dissolution process, with loss of thermal and process history of the samples. The film samples must be randomly oriented, because nonrandom chain orientation influences the absorption intensity measured.

2.1.4 Quantitative IR Spectroscopy of Polymers

IR spectroscopy is routinely employed to estimate an identity and the concentration of absorbing species in multicomponent systems. The standard approach is to measure the spectral series of mixtures, as well as using simultaneous equations to extract the desired information on concentration. There are four different classes of spectral problems in the analysis of multi-component systems. In the first case that all of components in the system are known and calibration data are available, classical least-square method is appropriate for determining quantities of each component. When a proper calibration method is carried out, this approach yields quantitative data for mixtures with high accuracy. In the second situation, the spectra of components are unknown but concentrations of components of interest are known, uses of a cross-correlation procedure are needed. In the third situation, when none of any components are known, factor analysis can be applied very well. Factor analysis method provides a lower limit to the number of linear-independent components presenting in a mixture, and estimates the spectra when low numbers of components (less than three) are presented. Finally, to quantify a number of known components in a presence of a variable background of unknowns is the most difficult situation. In an attempt to handle such a problem, method of rank annihilation has been developed. When there is only one known component, amount of the component can be determined by iteratively subtracting it from the observed data until the rank of the remaining matrix is reduced by one.

$$A = abc \ \ \log \frac{I_0}{I} \tag{2.1}$$

The quantitative relationship between a concentration (c) of a component in a sample and its absorbance (A) is given by the Bouguer-Beer law:

where I_0/I is termed transmittance. The constant a is an absorptivity, and b is thickness. Logarithms to the base 10 are ordinarily used, and a factor of 2.3 is incorporated into the constant a. This law assumes photometric linearity and accuracy of the spectrometer. Traditionally, constructing a calibration curve of absorbance of an analytical frequency versus the concentration can carry out quantitative purpose by measuring the concentration of an unknown sample in either term of the absorbance peak or the absorbance area. When two components are involved, absorbance measurements at two frequencies are necessary to estimate the individual concentrations. This method can be extended for systems with more components as well.

When multi-component, are under investigation, it is assumed that total signal, $y_T(\nu)$, for each component is a linear combination of the individual responses of the m components:

$$y_T(\nu) = y_1(\nu) + y_2(\nu) + y_3(\nu) + \ldots + y_m(\nu) \tag{2.2}$$

This equation represents the additivity assumption. It is also assumed that the individual response with respect to concentration, c_i, where i =1,…, m is linear, so

$$A_s^{\nu x} = A_2^{\nu x} - k' A_1^{\nu x} \tag{2.3}$$

and a_i are the sensitivity coefficient for the i^{th} component at the ν^{th} frequency. This equation reflects the linearity assumption.

For an analysis of multicomponent systems, it is necessary to use an analytical method to investigate whether the prerequisites of the additivity for signal responses or linearity of the absorption intensity. This can be practically accomplished by measuring the signal responses of each pure component and those of synthetic mixtures. The numerical sum expected can be compared with the experimental absorbances to test the additivity assumption. Linearity of the spectral intensity can be examined via the absorbance response of each pure component at the component-specific wavelengths for several different concentrations involving the other components. If specific interactions take place between the components, nonlinearity of responses will be appeared as a result [8].

2.1.5 Spectral Subtraction

Spectral subtraction with such versatile utilities has been become an important tool for spectroscopic analysis. Spectral subtraction allows studies of solid samples with a high precision by correlation of different sample thickness. Interferences on peaks of interest (i.e., those of artifacts, solvents, and other impurities) have to be removed in order to get pure sample spectra in the final before data analysis.

Computerized spectral subtraction permits an interference to be removed without a reference of precisely the same optical thickness. In practical two single-beam spectra are initially collected (i.e., those of the sample and whether other of the pure solvent or matrix whose spectrum is to be compensated). Both spectra are ratioed against a blank (no cell) reference, and finally absorbance spectra are achieved. Different effective pathlengths can be compensated by multiplying the reference spectrum by a factor *k*, and subtracting the scaled reference spectrum from the sample spectrum. The scaling factor *k* for interference band is calculated such that:

$$\left(A_1 - kA_2\right) = 0 \tag{2.4}$$

where A_1 is the absorption intensity of the sample peak, and A_2 is the absorption intensity of the interference band in the reference spectrum. Eq. 2 states that band of interest in both the sample and reference spectra are forced to have the same optical thickness.

This is known as scaled absorbance subtraction. Methods for calculation of the scaling factor may include a visual comparison of whether peak intensity or integrated peak area, or even a least-square curve-fitting method. In several commercial programs for spectral analysis, the integrated area of selected peaks is calculated, with the scaling factor that is estimated from ratio of these areas. There are a few instances where this procedure may not be appropriate, especially in case of the matrix and analyte have co-overlapping bands. The best method by which spectral subtraction is executed is to isolate a single band of the components in both spectra and then calculate *k* based on these single bands. When the pure reference spectrum is achieved, the factor *k* should be applied for subtraction of the entire spectral series. The only conclusive test for accuracy of the operation is a careful examination of the difference spectrum. If either the interference or component bands still persist after removal, or the final peak becomes somewhat negative, the factor *k* must be re-scaled.

Spectral subtraction is not only applied for removing interference. Koenig has established the principal uses of absorbance subtraction [9]. A simple confirmation of the identity of a sample has been become the first consideration. If a reference spectrum is subtracted from a sample spectrum and the final result is zero, it is clear that those two spectra are the same compound. In fact, this method is not explicitly implemented in spectral search systems because it is somehow too cumbersome; although but it is viable for authentication of a sample. This is probably the best test for unequivocally matching sample and reference spectra.

Quality control is ranked as the second principal of scaled absorbance spectral subtraction. If a standard spectrum of a product with known compositions is recorded, it can be employed as a reference for the subsequent product. In this case, the scaling factor is set to 1, and the final difference spectra should show positive or negative bands in order to indicate either an excess or deficiency of particular components. Tolerance limits should be set for deviations from the standard, used as the consideration in the procedure of quality assurance.

As mentioned above, scaled absorbance subtraction can be applied for removing impurities, solvents, or even major components. In this way, bands of interested constituents may be isolated. As a consequence, accurate peak assignments have to be first accomplished; though unexpected contaminants may be discovered as parts of the normal procedure.

The final application use of scaled absorbance subtraction is to investigate molecular changes. In this case, a sample spectrum is first recorded before that of measured and the sample subjected to a reaction (such as photolysis, adsorption of a gas, temperature change, and so on). Basically, a resulted difference spectrum indicates molecular changes as constant features by the subtraction method. Small spectral differences are easy to be determined by this method. New bands would occur as positive bands, and on the other hand, negative bands indicate as molecular structure disappeared under such an operating condition. Bands with derivative peak shape appear when the bands shifts slightly during the operation which is cause by changes in environment of an infrared chromophore.

Absorbance subtraction is based on two fundamental assumptions. First, it is assummed that the absorbance and shape of a band do not change with the optical thickness. Generally, the absorbance values must be less than 1 in order to meet this requirement. The assumption must be tested with every subtraction. If the residual absorbance after a subtraction has a different shape other than the original band shape, the assumption has been consequently violated, and the data analysis should be proceeded with nonlinearity methods. The second assumption is that a component in a mixture must have the linear interaction with each other differently at a relative concentration. Concentration-dependent interactions cause frequency shifts and band-shape changes, but there are rarely observed in solids. Spectral subtraction is applicable only to spectra obtained in the absorbance unit. In another word, spectra plotted in the transmission mode are exponential in nature rather than linear, and these should never be digitally subtracted.

2.1.5.1 Spectral Subtraction for Degradation Studies of Polymers

Because of high *S*/*N* ration and frequency accuracy as advantages of the FT-IR technique, absorbance subtraction can be employed as a sensitive method for detecting small changes in a sample during the degradation process. The common features in the spectral series are canceled and only changes are recorded.

Interfering absorption treatment [6], for spectrum 1, the following equation may represent the total absorbance ($A^{v}{}_{T1}$) of all components (x, y, z) at a frequency v.

$$A^{v}{}_{T1} = A^{v}{}_{x1} + A^{v}{}_{y1} + A^{v}{}_{z1} \tag{2.5}$$

where A is the absorption intensity. A similar expression can be written for spectrum2:

$$A^{v}{}_{T2} = A^{v}{}_{x2} + A^{v}{}_{y2} + A^{v}{}_{z2} \tag{2.6}$$

The absorbance of subtracted spectra ($A^{v}{}_{s}$) at a frequency v is

$$A^{v}{}_{s} = A^{v}{}_{T2} - \mathrm{K}A^{v}{}_{T1} = \left(A^{v}{}_{x2} - kA^{v}{}_{x1}\right) + \left(A^{v}{}_{y2} - kA^{v}{}_{y1}\right) + \left(A^{v}{}_{z2} - kA^{v}{}_{z1}\right) \tag{2.7}$$

where k is adjustable scaling parameter. In an attempt to remove the absorbance due to component x, it can be rewritten as

$$A^{v}{}_{x2} - kA^{v}{}_{x1} = A^{v}{}_{xs} = 0$$

or

$$K = \frac{A^{v}{}_{x2}}{A^{v}{}_{x1}} \tag{2.8}$$

Therefore, the difference absorbance will be as equation 2.9 without any characteristics of component x.

$$A^{\nu}{}_{s} = \left(A^{\nu}{}_{y2} - kA^{\nu}{}_{y1}\right) + \left(A^{\nu}{}_{z2} - kA^{\nu}{}_{z1}\right) \qquad (2.9)$$

By comparing stability of functional group, a polymer molecule normally contains several different functional groups with different stabilities. Sometimes the least stable group may degrade very fast and additionally initiate the degradation of another functional group. FT-IR technique can rank the stability of each the functional group presenting in a polymeric material. If two functional groups (i.e., x and y) decrease their IR spectral absorbance at their characteristic frequencies v_x and v_y, the difference absorbances of each functional group can be expressed as

$$A_s^{\nu x} = A_2^{\nu x} - k' A_1^{\nu x} \qquad (2.10)$$

and

$$A_s^{\nu y} = A_2^{\nu y} - k' A_1^{\nu y} \qquad (2.11)$$

In a usual absorbance subtraction experiment, sample thickness and extinction coefficient are assumed to be constant throughout the measurement. Setting $k' = 1$ thus gives changes in concentration of the functional group absorbing at each wavenumber. However, varying k' is another way to force the intensity difference at a certain wavenumber to be zero, for example:

$$A_s^{\nu x} = A_2^{\nu x} - k' A_1^{\nu x} = 0 \qquad (2.12)$$

or

$$k' = \frac{A_2^{\nu x}}{A_1^{\nu x}} \qquad (2.13)$$

With this value of k', $A^{\nu}{}_{s}$ can be achieved. One finds that $A^{\nu}{}_{s}$ is either greater than, equal to, or less than zero which indicates that functional group y is either more stable than, as stable as, or less stable than the functional group x, respectively. This simple approach for absorbance subtraction, so called the relative functional group stability approach, is useful for spectral analysis of polymer degradation. The calculation may be applied to functional groups of species formed as reaction products as well.

2.2 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is the technique that observes changes in sample mass (mass-loss or gain) as a function of temperature and/or time. Three modes of thermogravimetric analysis, as illustrated in Figure 2.2, are commonly utilized: (*a*) isothermal thermogravimetric analysis, in which the sample mass is recorded as a function of time at constant temperature. (*b*) quasi-isothermal thermogravimetric analysis, in which the sample is heated to a constant mass at each series of increasing temperatures; and (*c*) dynamic thermogravimetric analysis, in which the sample is heated in an environment whose temperature is changing in a predetermined manner, preferably at a linear rate [10].

The observed curve of mass change versus temperature (so called thermolysis curve, pyrolysis curve, thermogram, thermogravimetric curve, thermogravigram, thermogravimetric analysis curve, and so on) provides information on the thermal stability and composition of the initial sample, the thermal stability and composition of any intermediate compounds formed, and the composition of the residue, if any. Characteristics of a single-stage mass-loss curve are illustrated in Figure 2.3.

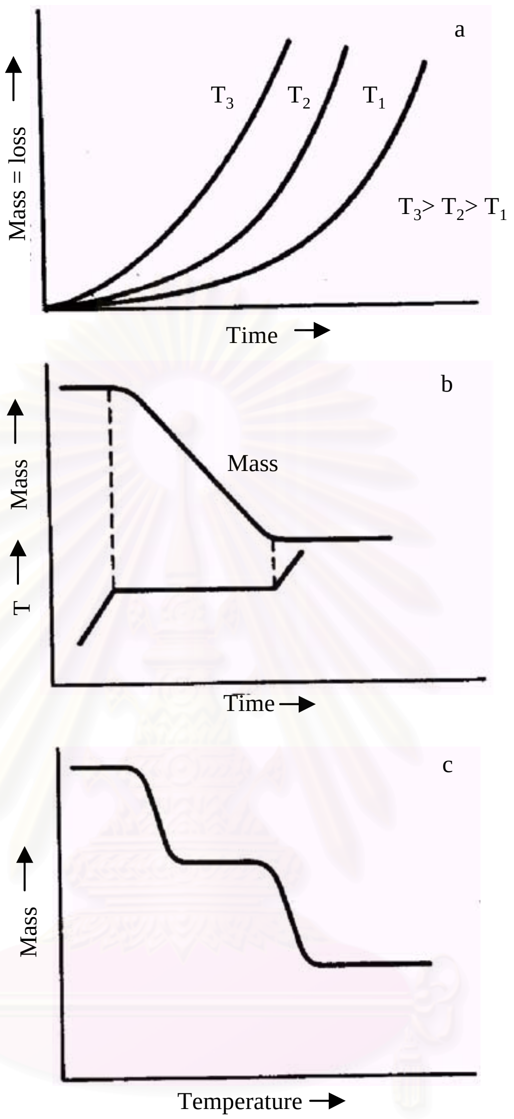
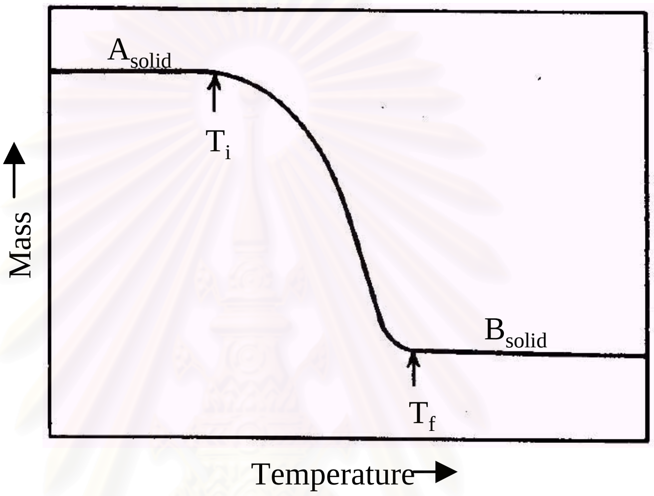


Figure 2.2 Three modes of thermogravimetric analysis. (*a*) isothermal thermogravimetric analysis, (*b*) quasi-isothermal thermogravimetric analysis, and (*c*) dynamic thermogravimetric analysis.

Two temperatures may be selected as characteristics of any single-stage non-isothermal reaction: T_i, is the initial temperature or procedural decomposition temperature (pdt), which is the temperature at which the commulative mass-change reaches a magnitude that the thermobalance can detect; whereas T_f is the final temperature, where the commulative mass-change first reaches its maximum value corresponding to complete reaction. Although T_i may be the lowest temperature at which the onset of a mass-change may be observed in a given experiment, it is neither a transition temperature in the sense of phase rule nor a decomposition temperature below, which the reaction rate suddenly becomes zero. At a linear heating rate, T_f must be greater than T_i, and the difference of T_f - T_i is called the reaction interval. For an endothermic decomposition reaction, both T_i and T_f increase with increasing heating rate. The effect is greater for T_f than that for T_i.



$$A_{(solid)} \longrightarrow B_{(Solid)} + C_{(Gas)}$$

Figure 2.3 Characteristics of a single-stage reaction TGA curve.

The thermal stability is defined as a general term indicating the ability of a substance to maintain its properties as nearly unchanged as possible on heating. From a practical point of view, thermal stability needs to be considered in terms of both the environment to be imposed on the material and the functions its has to perform. The thermobalance is a useful technique for studying the ability of a substance to maintain its mass under a variety of conditions.

2.2.1 Derivative Thermogravimetric Analysis (DTGA)

In conventional thermogravimetric analysis, the mass of sample (*m*) is continuously recorded as a function of temperature *T* or time *t*;

$$m = f\left(T \text{ or } t\right) \tag{2.14}$$

Quantitative measurements of mass changes are possible with measurement of the distance on the curve mass axis whether between two points of interest or between two horizontal mass levels. According to basics of derivative thermogravimetric analysis, derivative of the mass-change with respect to time, *dm*/*dt*, is recorded as a function of time (*t*) or temperature (*T*) as expressed:

$$\frac{dm}{dt} = f\left(T \text{ or } t\right) \tag{2.15}$$

In other cases, the derivative of the mass-change with respect to temperature, *dm*/*dt*, is recorded as a function of time (*t*) or temperature (*T*),

$$\frac{dm}{dT} = f\left(T \text{ or } t\right) \tag{2.16}$$

In either case, the resulting curve is the first derivative of the mass-change curve. A series of peaks are obtained, instead of the stepwise curve, with area under the peaks that are proportional to the total mass-change of the sample. A horizontal plateau in a TGA curve gives a corresponding horizontal plateau in the DTGA curve where *dm*/*dt* = 0. A maximum in the DTGA curve is observed when the TGA curve has an inflection point where mass is lost most rapidly.

A comparison between a conventional (*a*) and a derivative (*b*) mass-loss curve is present in Figure 2.4. The derivative curve may be obtained either from the TGA curve by manual differentiation methods or by electronic differentiation of the TGA signal. Accessory equipment is available for most thermobalances so that the

DTGA curve can be easily recorded along with the TGA curve. The DTGA curve, whether derived mathematically or recorded directly, contains no more information than that with an integral TGA curve obtained under the same experimental conditions. They simply display data pattern differently.

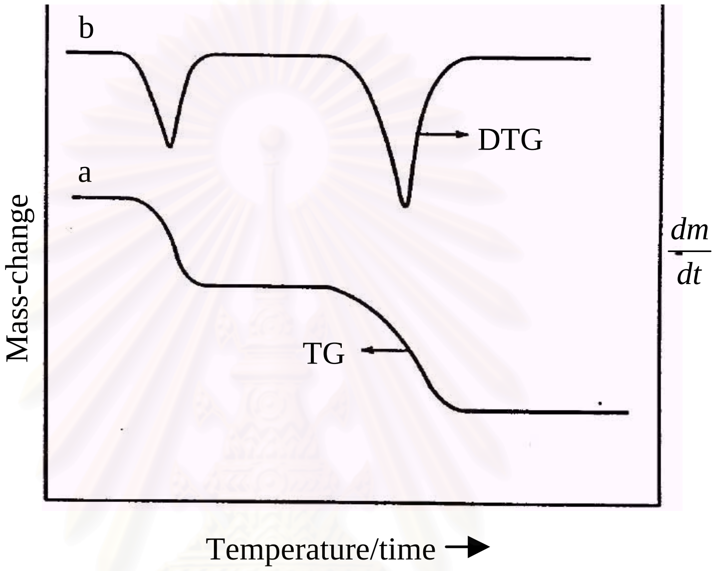


Figure 2.4 Comparison between integral (TGA, *a*) and derivative (DTGA, *b*) mass-loss curves.

Information obtainable from DTGA curve has been summarized by Dunn [10]:

- The DTGA curve presents the information in a form that is more visually accessible, whereas the DTGA curve contains no more information than the TGA curve does.
- The DTGA curve allows a ready determination of the temperature at which the rate of mass-change is a maximum, T_{max}, and this provides additional information to the extrapolated onset temperature $T_{e,}$ and the extrapolated final temperature T_f. All three temperatures, however, respond to changes in experimental conditions, and T_{max} values are no more characteristic of a material than is T_i or T_f.

- Area under a DTGA curve is directly proportional to the mass-change.
- Height of a DTGA peak at a certain temperature gives the rate of mass-change at that temperature. These values can be utilized to obtain kinetic information since equations can be written in forms of:

$$-\frac{dm}{dt} = Ae^{(-E/RT)} f(m) \tag{2.17}$$

Dunn has discussed applications of the DTGA curve for thermogravimetric analysis including:

- Separation of overlapping reactions, reactions occurring within the same temperature range result in TGA curves that appear as one continuous mass-loss. However, DTGA curves are discontinuous lines, and hence subtle mass-changes are emphasized. Four different TGA curves and their corresponding DTGA curves are shown in Figure 2.5. Curve (*a*) is a single reaction that occurs over a small temperature range. Curve (*b*) consists of two reactions that are partially overlapping; curve (*c*) consists of two reactions, the first of which occurs slowly, followed by a fast reaction; and curve (*d*) is one in which minor reactions occur during or near a major reaction.

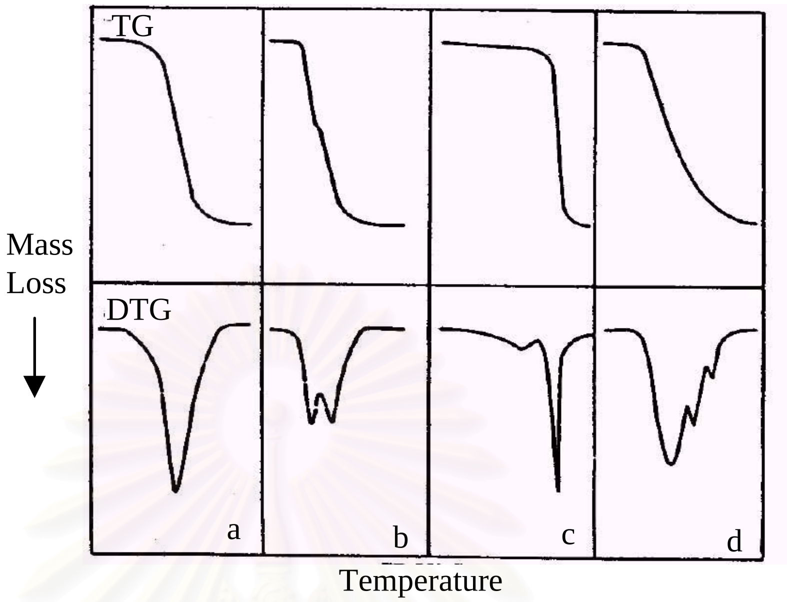


Figure 2.5 Comparison of TGA and DTGA curves. Three of which exhibit overlapping reactions.

- Fingerprinting materials because the subtleties of a TGA curve are visually emphasized in the DTGA curve, the latter are frequently recorded as parts of the characteristic information collected on newly unknown, or standard material.

- Calculation of mass changes in overlapping reactions. When overlapping reactions occur, it is sometimes difficult to locate on the TGA curve an unambiguous point where a reaction ends and another starts. Using the minimum in the DTGA curve, an extrapolation procedure, such as that shown in Figure 2.6, can be performed to determine approximately where the second reaction begins.

- Quantitative analysis by peak height measurement. Peak heights on DTGA curve may be used for quantitative purposes since when no mass-loss is occurring (i.e., $dm/dt = 0$). During a mass-loss reaction where $dm/dt > 0$ the DTGA peak is proportional to the mass-loss of sample.

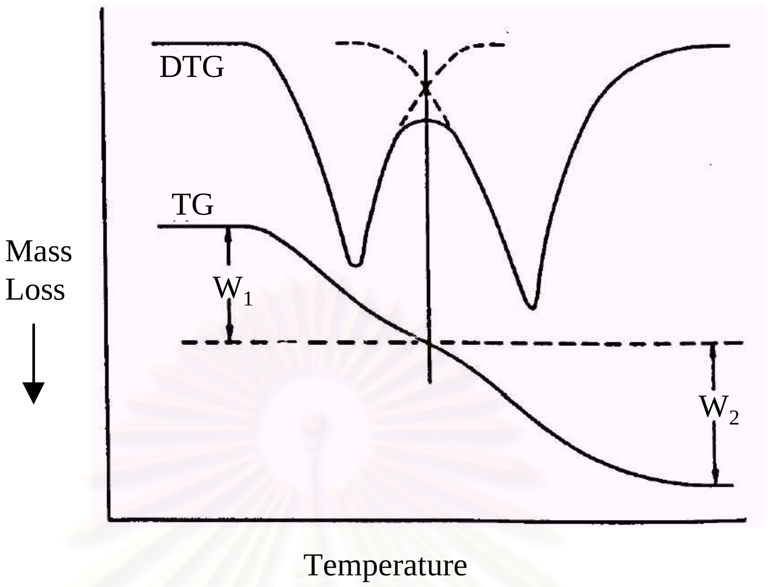


Figure 2.6 Idealized TGA and DTGA curves in which the minimums in the DTGA curve is used to define the end of the first mass-loss and the onset of the second.

In addition, the advantages of derivative thermogravimetric analysis have been summarized by Erdey *et. al*.:

- The curves may be obtained in conjunction with TGA and DTA measurements.
- The curves for DTA and derivative thermogravimetric analysis (DTGA) are comparable. But results of the former method indicate even those changes of state that are not accompanied by loss in mass, whereas the latter method gives more reproducible curves.
- Although the DTA curves extend over a wider temperature interval due to subsequent warming of the material after reaction, the DTGA measurements indicate exactly the temperatures of the beginning, the maximum rate, and the end of changes.
- With TGA method, changes following each other very closely cannot be distinguished, as the corresponding stages coincide. The DTGA curves of the same change indicate by sharp maxima that the thermogravimetric stages can be devided into two parts.

-DTGA curves are exactly proportional to the derivatives of the TGA curves: As a result, the area under the curves gives the change in mass precisely. Accordingly, DTGA can give exact quantitative analyses.

-The DTGA method can be performed for investigation of materials which for some reason or another cannot be analyzed by DTA. For example, some organic compounds melt during heating, but even so the DTGA method yields fairly good results.

2.2.2 Applications of Thermogravimetric Analysis

This technique involves continuous weighing of a polymer as it is subjected to a temperature programme. The technique can itself provide quantitative information about kinetics of the thermal decomposition of polymeric material from which the thermal stability of the polymer can be evaluated. It is employed to study influences of some factors on polymer degradation. Such factors include effect of crystallinity, molecular weight, orientation, tacticity, substitution of hydrogen atoms, grafting, copolymerization as well as the addition of stabilizers.

The lifetime or shelf-life of a polymer can be estimated from these kinetic data. Ozawa, Flynn, and Wall observed that the activation energy of a thermal event could be determined from a series of thermogravimetric runs performed at different heating rates. As the heating rate increased, the thermogravimetric changes would take place at higher temperatures. A linear correlation was obtained by plotting the logarithm of either the heating rate or scans speed against the reciprocal of the absolute temperature at the same conversion or weight loss percentage. The slope was directly proportional to the activation energy and known constants. To minimize errors in calculation, approximations were added to calculate the exponential integral. It was assumed that the initial thermogravimetric decomposition curve (2-20% conversion) obeyed the first-order kinetics. Consequently, rate constants and pre-exponential factors could be calculated and used to examine relationships between temperature, time and conversion level [11]. The thermogravimetric decomposition kinetics could be applied for such calculations:

- Lifetime of the sample at certain temperatures.
- Temperature corresponding to a certain lifetime.
- Lifetimes at all temperatures with a known percentage conversion.

CHAPTER 3

EXPERIMENT

3.1 Preparation of Ternary Systems and Terpolymer

3.1.1 Materials

Benzoxazine resin was synthesized based on the traditional method from bisphenol A and aniline type i.e., 2,2´-(3-phenyl-4-dihydro-1,3,2-benzoxazine)propane, BA-a. The diglycidyl ether of bisphenol A epoxy resin, Epon 825, from Shell Chemicals, was used as received without further purification. The resin is a clear viscous liquid at room temperature. The resin contains an epoxide content of 173 to 179 mol/kg. Phenolic novolac, HRJ1166, was obtained from Schenectady International. The resin is a dark red solid at room temperature. All materials were kept in closed containers at room temperature.

3.1.2 Sample Preparation

Each resin was first mixed at a desirable mass fraction. The mixture was then heated to about 80 ^{o}C in an aluminum pan and was stirred by hand for a few minutes until the homogeneous mixture was obtained. In order to receive the fully cured resin, the obtained mixture was heated at 200^{o}C for 2 hrs. in the oven.

In the nomenclature of binary and ternary mixtures, the letter B, E, and P stand for benzoxazine, epoxy and phenolic resins, respectively. Three numbers that follow the abbreviation are the mass ratio of the resins i.e., BEP 514 represents benzoxazine, epoxy, and phenolac mixture with the mass ratio 5:1:4, respectively.

In this research, BEP514 was represented for study the degradation of ternary system. This is due to BEP514 exhibit high thermal stability as reported in the research of Rimdusit and Ishida [2].

3.2 Thermal Degradation

3.2.1 TGA Analysis

3.2.1.1 Chemicals and Equipment

1. Polybenzoxazine (B)
2. Cured epoxy (E)
3. Phenolic novolac resin (P)
4. Copolmer of benzoxazine and epoxy (BE)
5. Copolymer of benzoxazine and phenolic novolac (BP)
6. Terpolymer of benzoxazine, epoxy, and phenolic novolac (BEP514)
7. Netzsch STA 409 C Thermogravimetric Analyzer

3.2.1.2 TGA Analyzer conditions

Experimental Setup

Weight of Sample:	10 mg
Heating Rate:	$20^{o}C/min$
Environment:	N_2 Atmosphere
Heating Temperature:	$30^{o}C-900^{o}C$

3.2.2 FT-IR Technique

3.2.2.1 Materials and Equipment

1. Polybenzoxazine: B
2. Epoxy: E
3. Phenolic novolac resin: P
4. Copolmer of benzoxazine and epoxy (BE)
5. Copolymer of benzoxazine and phenolic novolac (BP)
6. Terpolymer of benzoxazine, epoxy, and phenolic novolac (BEP514)
7. Potassium bromide (KBr) powder
8. Bruker Vector 33 FT-IR Spectrometer

3.2.2.2 FT-IR Spectrometer Conditions

Experimental Setup

Resolution: 4.0 cm^{-1}
Number of Scans: 32
Result Spectrum: Absorbance

Optic Parameters

Source Setting: Globar (MIR)
Detector Setting: DTGS
Beam Splitter Setting: KBr

3.2.2.3 Spectral Acquisitions

The sample-KBr pellets were prepared as followed, grinding 0.5-1.5 mg sample into a small powder using agate mortar then adding 100-200 mg of KBr powder. The mixture are placed into a mould and pressed under high pressure to produce a transparent pellet. The sample was then mounted on a sample holder, which was located in a hot cell to maintain the reaction temperature.

For non-isothermal analysis, the samples were examined at 230 ^{o}C to 500 ^{o}C. Spectra were collected as absorbance spectra every 1 min. The isothermal analysis was performed with only BEP514 at 300, 330 and 360 ^{o}C. The spectra were recorded every 5 minutes for a total period of 3 hours.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Thermal Degradation of Polybenzoxazine, Epoxy Resin, Phenolic Resin

Polybenzoxazine, a class of thermosetting phenolic resin, has unique advantages of high glass transition temperature (T_g), high thermal stability, good mechanical property, and flexibility on molecular design. Structure of polybenzoxazine is in form of a phenolic resin structure characterized by a Mannich based bridge (-CH_2-NR-CH_2-), as shown in Figure 4.1. The FT-IR spectrum of polybenzoxazine is shown in Figure 4.2. The peak assignment of polybenzoxazine is shown in Table 4.1.

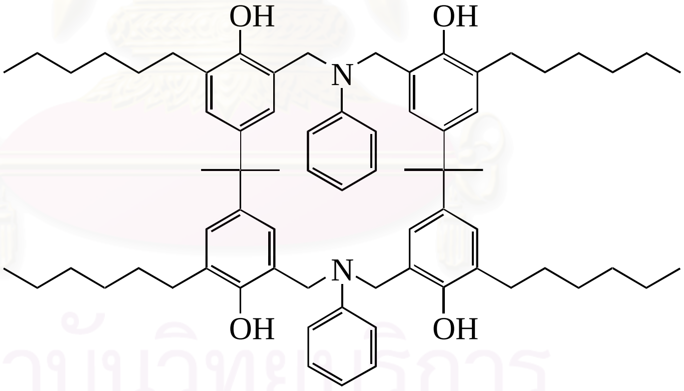


Figure 4.1 Chemical structure of polybenzoxazine.

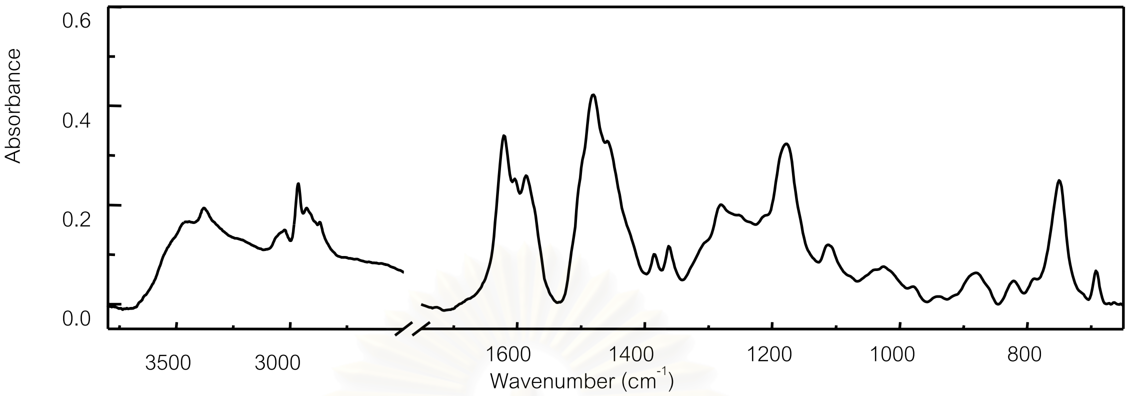


Figure 4.2 FT-IR spectrum of polybenzoxazine.

Table 4.1 FT-IR band assignments of polybenzoxazine

Peak Position (cm^{-1})	Peak Assignment
3400	O-H of phenol
3026	C-H stretching of benzene ring
2965	C-H asymetric stretching of methylene group
2930	C-H asymetric stretching of methylene group
2870	C-H symetric stretching of methylene group
1620, 1583, 1478	C=C stretching of benzene ring
1382	C-H asymetric deformation of geminated methyl group of bisphenol A
1362	C-N (-Ar) asymetric stretching of aliphatic aromatic amine
1278	C-N stretching of aromatic amine
1182	C-C stretching in Ar-C(-C)-Ar
1115	C-N stretching of aliphatic amine
881	C-H out of plane vibration in term of isolate hydrogen atom of 1, 2, 3, 5-tetra-substitued benzene
824	C-H out-of-plane deformation of 1,2,3,5-tetra-substituted benzene ring of phenolic resin
754, 694	C-H out of plane deformation mono-substituted mode of benzene ring

The chemical structure of cured epoxy resin is shown in Figure 4.3, while Figure 4.4 shows, the FT-IR spectrum of cured epoxy resin. The peak assignment of FT-IR spectrum of cured epoxy resin is shown in Table 4.2.

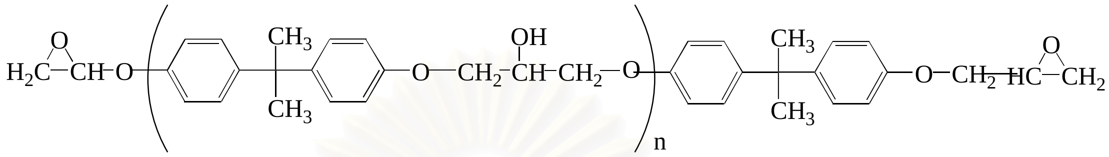


Figure 4.3 Chemical structure of cured epoxy resin.

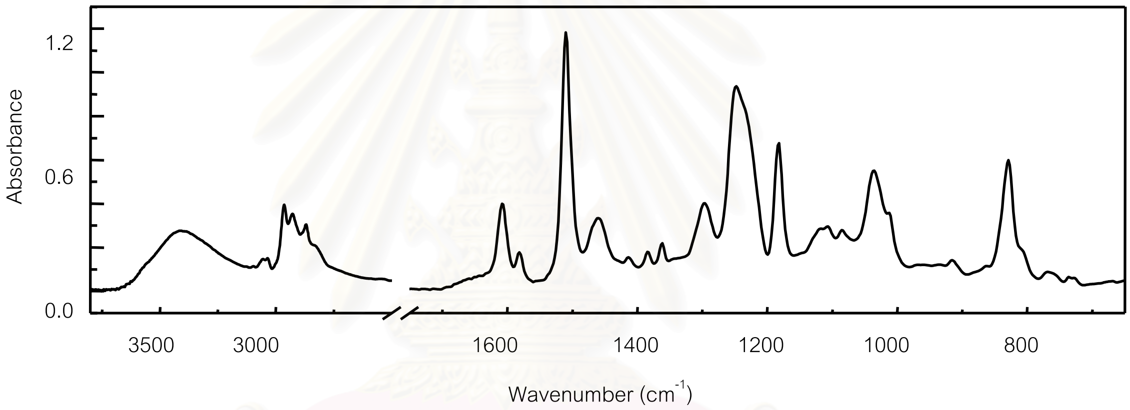


Figure 4.4 FT-IR spectrum of cured epoxy resin.

Table 4.2 FT-IR band assignments of cured epoxy resin

Peak Position (cm-1)	Peak Assignment
3404	O-H stretching of alcohol
3055	C-H asymmetric stretching of methylene of epoxide ring
3037	C-H stretching of benzene ring
2966	C-H asymmetric stretching of methyl group
2928	C-H asymmetric stretching of methylene group
2872	C-H symmetric stretching of methyl group
1608, 1582, 1512, 1462	C=C stretching of benzene ring
1384	C-H symmetric deformation of geminated methyl group of bisphenol-A
1298	C-O (-Ar) asymmetric stretching of aliphatic aromatic ether
1250	C-O(-C) symmetric stretching of epoxide ring
1184	C-C stretching in Ar-C(-C)-Ar
1109	C-O stretching of alcohol
1037	C-O-(-Ar) symmetric stretching of aliphatic aromatic ether
832	C-H out-of-plane deformation of *p*-di-substitued benzene

The chemical structure, FT-IR spectrum, and peak assignments of phenolic resin are shown in Figures 4.5, 4.6 and Table 4.3, respectively.

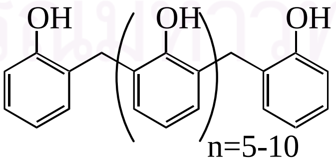


Figure 4.5 Chemical structure of phenolic resin.

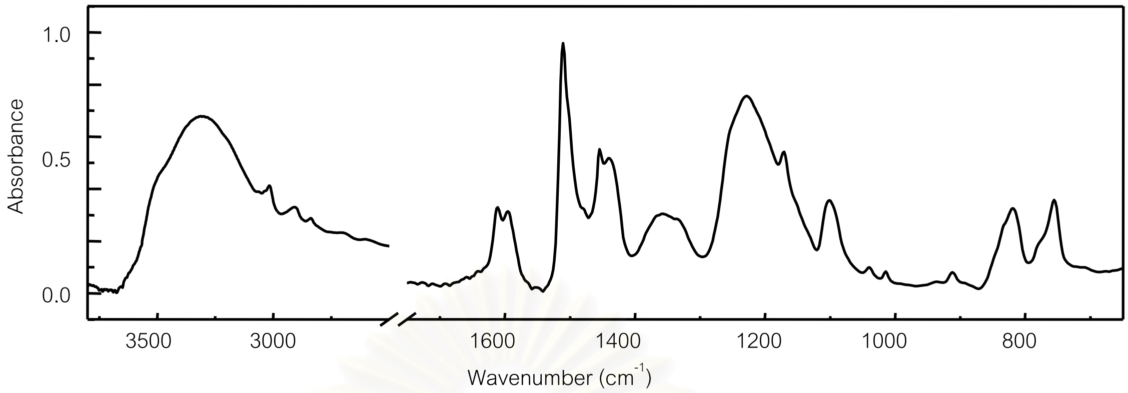


Figure 4.6 FT-IR spectrum of phenolic resin.

Table 4.3 FT-IR band assignment of phenolic resin

Peak position (cm^{-1})	Peak assignment
3332	O-H stretching of phenol
3018	C-H stretching of benzene ring
2905	C-H asymmetric stretching of methyl group
2842	C-H symmetric stretching of methylene group
1612, 1595, 1510, 1455	C=C stretching of benzene ring
1351	O-H in plane deformation of phenol
1228	C-O asymmetric stretching of phenol
1175, 1102	C-H in plane deformation of 1,2,3-tri-substitued benzene ring
822	C-H out-of-plane deformation of 1,2,3-tri-substitued benzene ring
760	C-H out-of-plane deformation of 1,2-di-substitued benzene ring

4.1.1 TGA Analysis

The TGA thermograms of polybenzoxazine, epoxy resin, and phenolic resin and derivatives are shown in Figures 4.7 and 4.8. Table 4.4 is the summary of Figures 4.7 and 4.8. The temperatures at 5 % weight-loss for these homopolymers are different. Phenolic resin is the least thermally Table compound, with an onset degradation temperature below 288 ^{o}C. Epoxy resin has the highest temperature at 5 % weight-loss at 337 ^{o}C. However, epoxy resin gives the least char yield (at 800 ^{o}C) with 10.47 % residue at 800 ^{o}C. Phenolic resin possess the highest char yield (800 ^{o}C) of 20.9 %. At present, the order of thermal stability (determined by 5 % weight-loss temperature) is epoxy resin > polybenzoxazine > phenolic resin. The order of char yield at 800 ^{o}C is phenolic resin > polybenzoxazine > epoxy resin.

According to Figure 4.8, the epoxy resin shows one major weight-loss under narrow temperature range of peak. This indicates a event for rapid degradation of epoxy resin under high temperature. Lin and co-workers studied degradation of epoxy resin and indicated that the isopropylidene group seems to be least Table in polymer chain of epoxy resin [6]. The isopropylidene group degrades and releases the CH_3 group at approximately 350 ^{o}C. From Figure 4.8, there are three major weight-loss events occur in polybenzoxazine. Low and Ishida used evolved gas analysis to determine the nature of these three weight-loss events [12]. The first event, with a maximum near 330 ^{o}C, designated to the breaking of Mannich bridge in the phenolic resin bridge network picture as depicted in Figure 4.9. The primary weight-loss product was free anilines released by de-aminomethylation [12]. The second weight-loss event, centered near 400 ^{o}C, was represented to the break-up of the isopropylidene linkage of the Bisphenol A backbone [12]. The primary weight-loss event, centered near 460 ^{o}C, was assigned to the degradation of char, with trace phenolic resin and significant amounts of substituted benzene compound being released [12]. The derivative curve of phenolic resin (Figure 4.8) shows more than three weight-loss events. The temperature range of degradation in phenolic resin is wide.

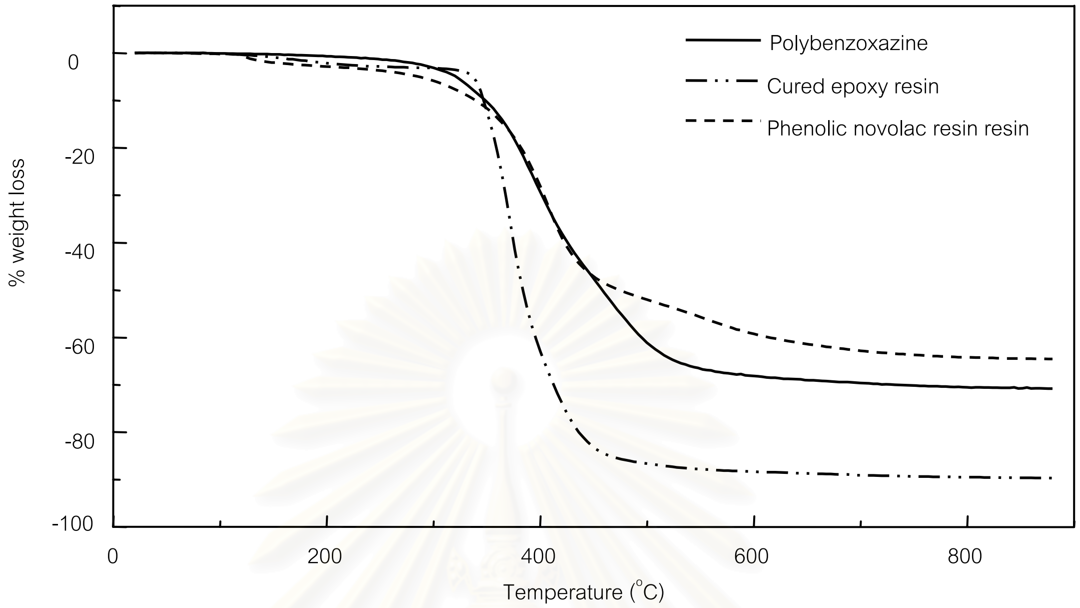


Figure 4.7 TGA thermogram of polybenzoxazine, epoxy resin and phenolic resin.

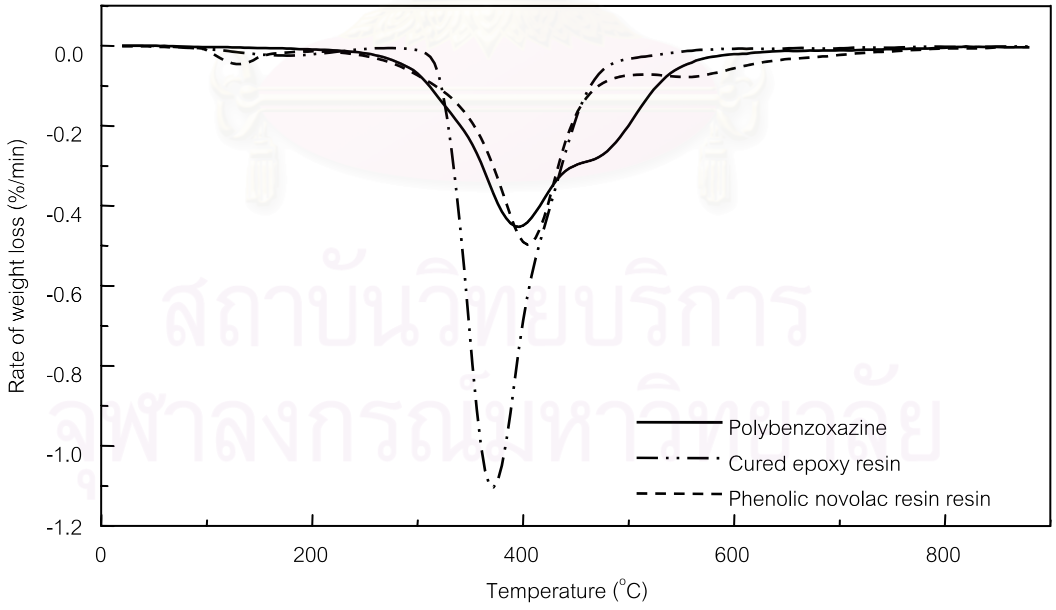


Figure 4.8 Derivatives of TGA thermogram for polybenzoxazine, epoxy resin and phenolic resin.

Table 4.4 Thermal properties of the homopolymers

Condition	Polybenzoxazine	Epoxy resin	Phenolic resin
-Temperature at 5% weight loss (^{o}C)	321	337	288
- Temperature at major peak (^{o}C)	395, 468	366	404, 555
- % Residue at 800^{o}C	29.42	10.47	35.79

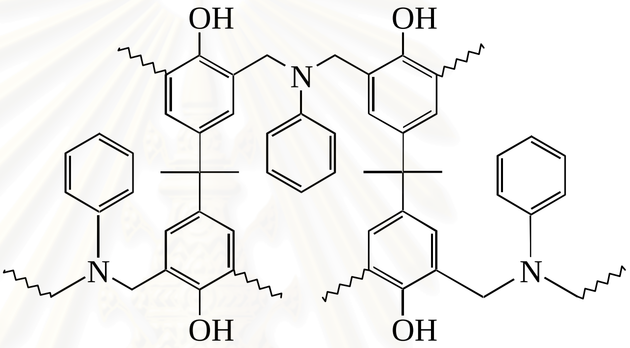


Figure 4.9 Mannich bridge network in phenolic resin.

4.1.2 FT-IR spectroscopy

The FT-IR spectra of thermal degradation of polybenzoxazine are shown in Figure 4.10. These spectra are presented as a function of temperature. The polybenzoxazine was degraded by heat as observed the spectral series with some changes as increasing temperature. The band at 1120 cm^{-1} is assigned to C-N stretching of Mannich base (C-N-C). The band intensity decreases with increasing temperature. Until at 435 ^{o}C, this band disappears. The cleavage of the C-N rather than C-C bond from the Mannich base can also be supported from the bond energy point of view. Since C-C bond has a higher dissociation energy than that of a C-N bond, the first stage of thermal degradation of polybenzoxazine is the Mannich base cleavage.

As a result, it is generalized that the first weight-loss event in the TGA thermogram of polybenzoxazine is assigned to the C-N cleavage. The second major weight-loss is a result of the degradation of phenolic resin. The mechanism of thermal degradation in the aniline-base polybenzoxazine is presented in Figure 4.10 and 4.11. It is noted that, for all the proposed degradation schemes, hydrogen atoms are available via radical abstractions. The discussion on the degradation mechanism will mainly focused on the Mannich base as reported in a previous study [12]. Figure 4.11 is proposed when the nitrogen of Mannich base is hydrogen-bonded. The hydrogen bonding results in a stable six-membered ring. There are two possible degradation routes from this figure. First, aniline is produced. The latter is the production of a stable conjugated Schiff base (C=N). Since the bond dissociation energy of a C-C bond is lower than that of C=N bond, a more likely cleavage site of this conjugated Schiff base is preferentially at the C-C bond. Figure 4.11 shows possible degradation routes for the cleavage of this C-C bond.

Figure 4.12 is proposed when the nitrogen of the Minnich base is not hydrogen bonded. Because of the dissociation energy of a C-N bond is lower than that of a C-aromatic bond, both C-N bonds in the Minnich base have equal probability of cleavage. Both degradation in Figure 4.11 and 4.12 produce aniline as a result.

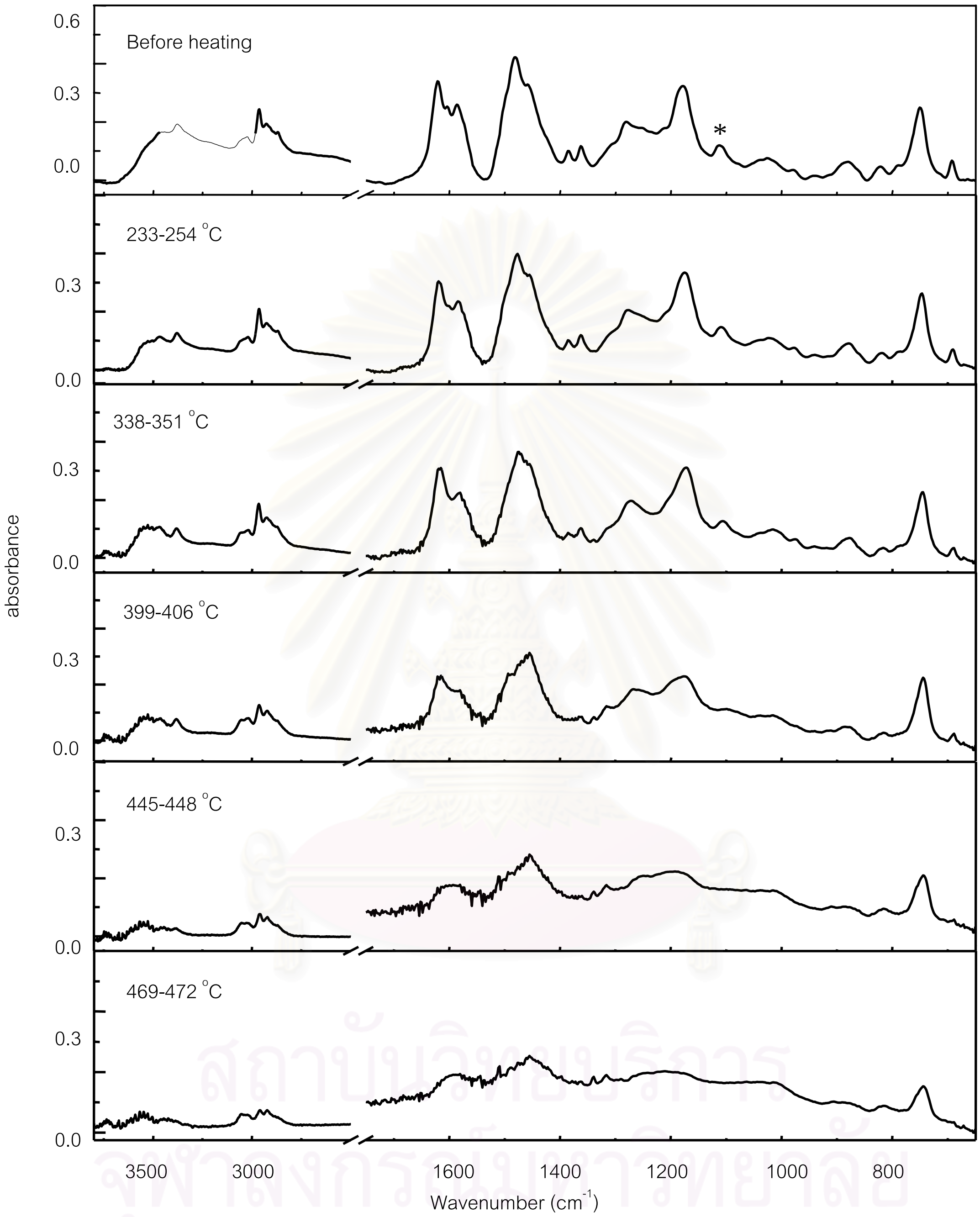


Figure 4.10 FT-IR spectra of thermal degradation of polybenzoxazine

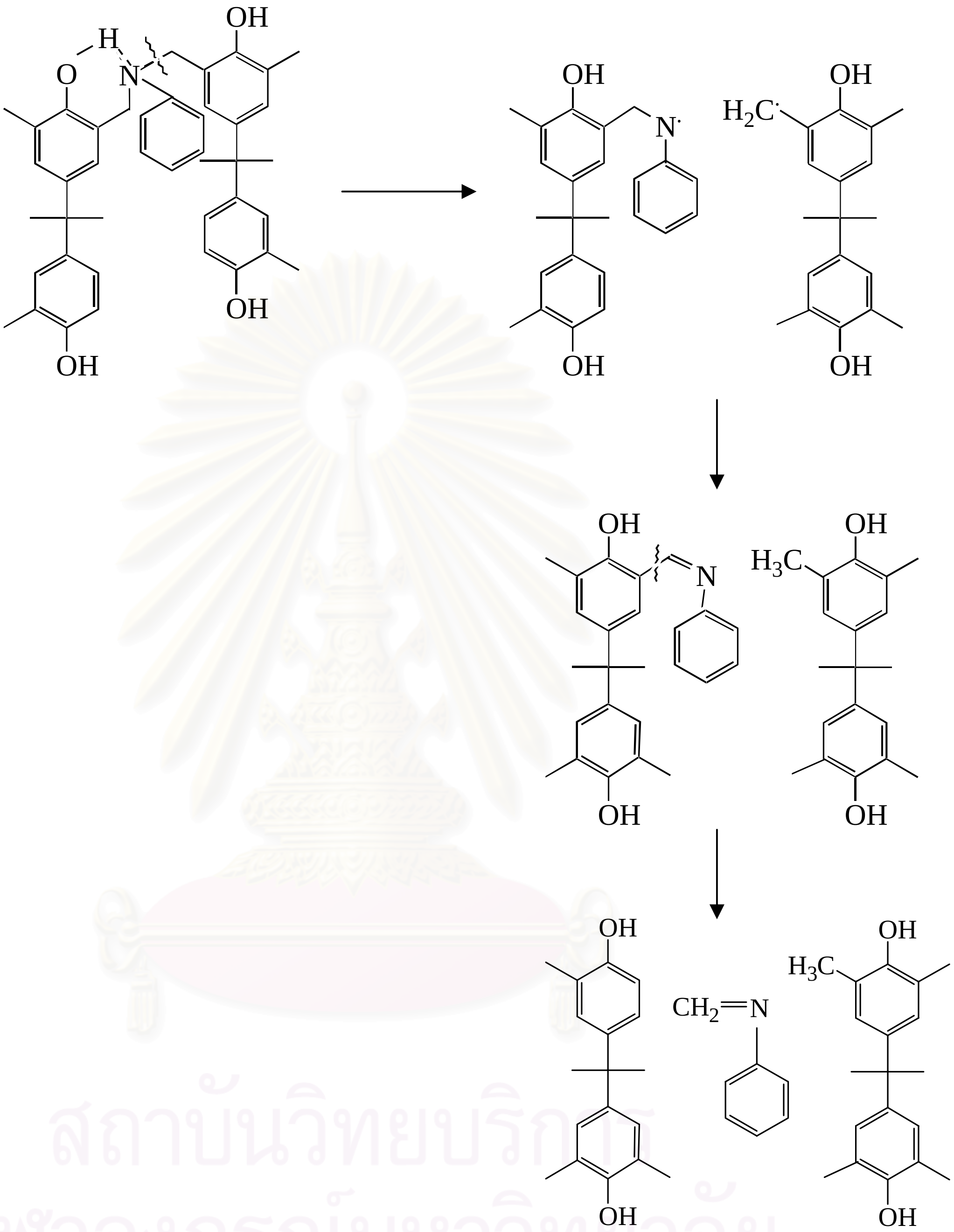


Figure 4.11 Proposed Mannich base cleavage in the presence of intramolecular hydrogen bond from polybenzoxazine.

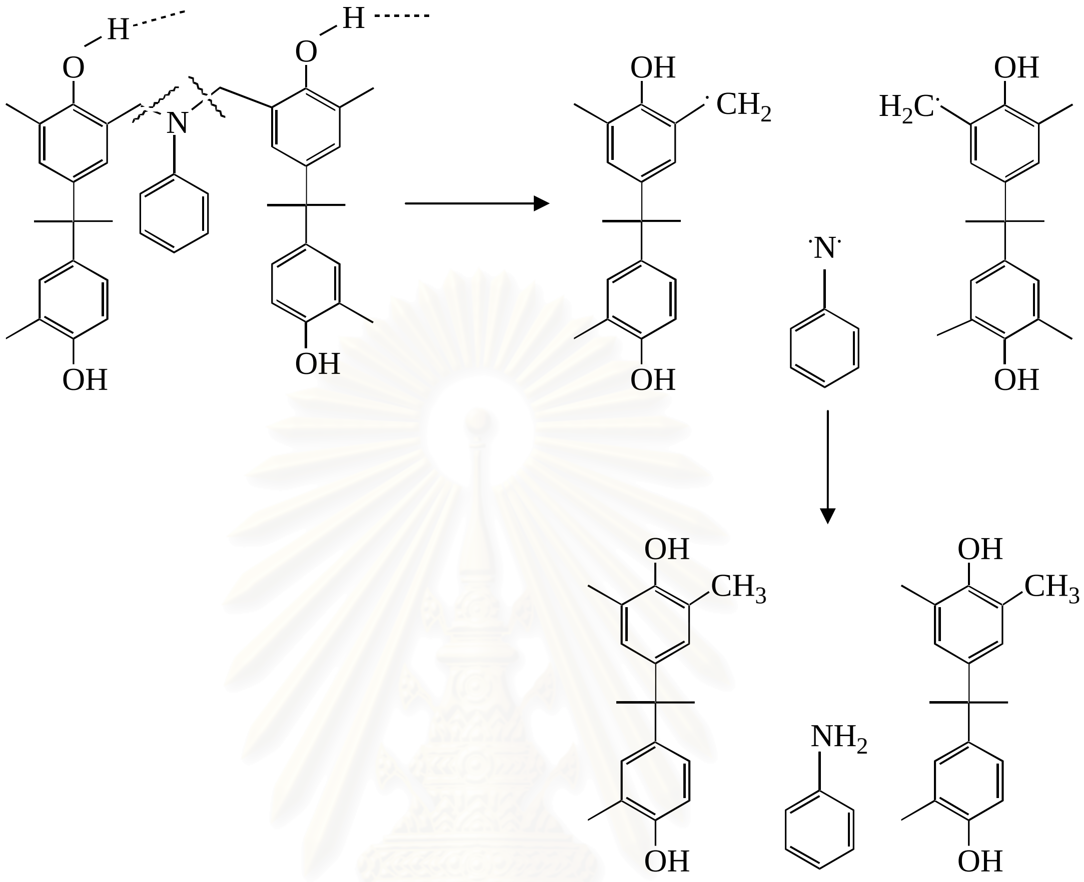


Figure 4.12 Proposed Mannich base cleavage in the absence of intra hydrogen bond from polybenzoxazine.

The FT-IR spectra of thermal degradation of cured epoxy resin are shown in Figure 4.13. These spectra are presented as a function of temperature. The band at 1184 cm^{-1} is assigned to the C-C bond of isopropylidene group. This band show a decrease in absorbance with increasing temperature until 430 ^{o}C, where these bands disappear. As reported elsewhere [6], the bond dissociation of isopropylidene group occurs during the decomposition process (see Figure 4.14). Base on the association energy, $C-CH_3$ bond in the isopropylidene group has a low bond energy.

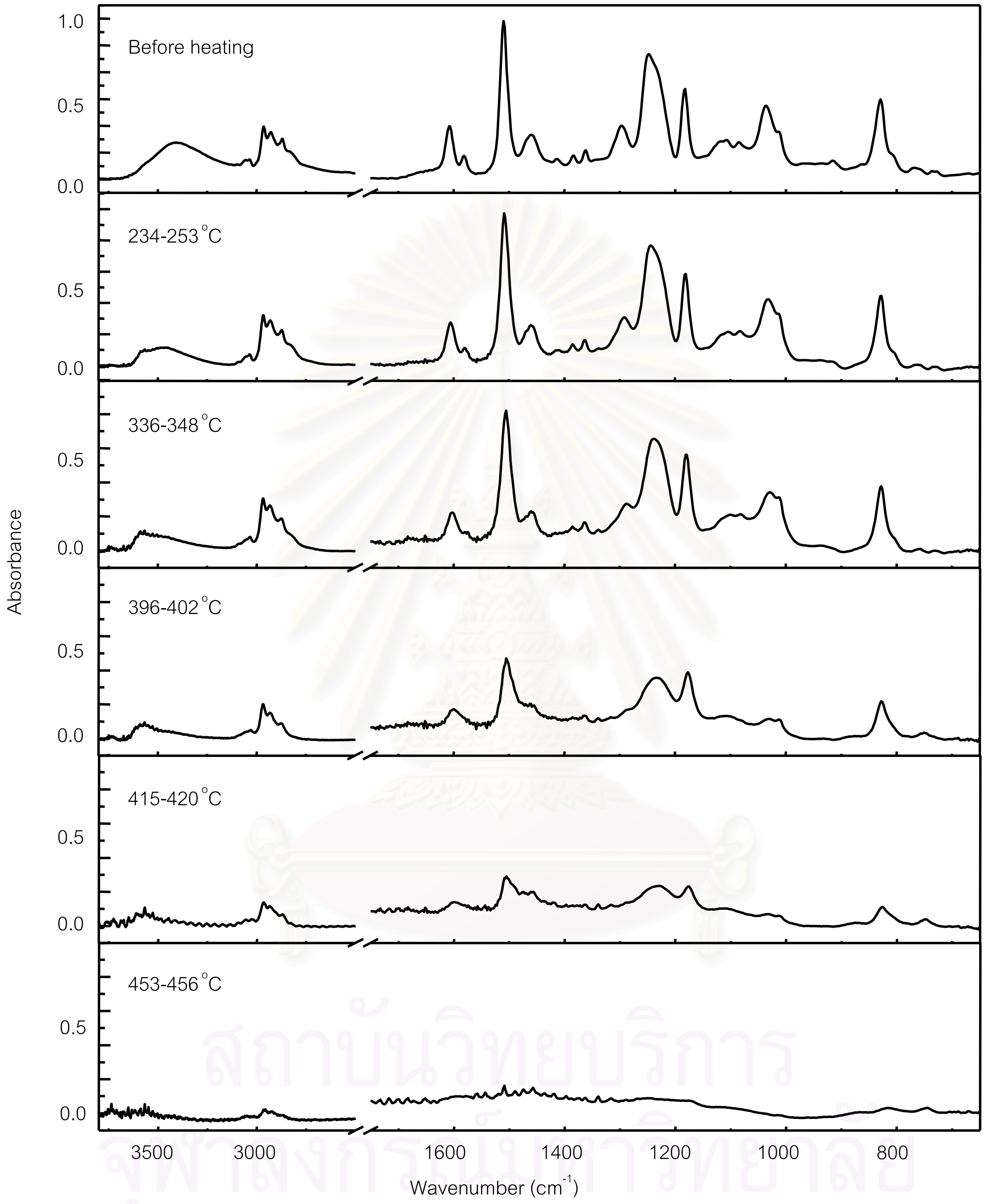


Figure 4.13 FT-IR spectra of thermal degradation of cured epoxy resin.

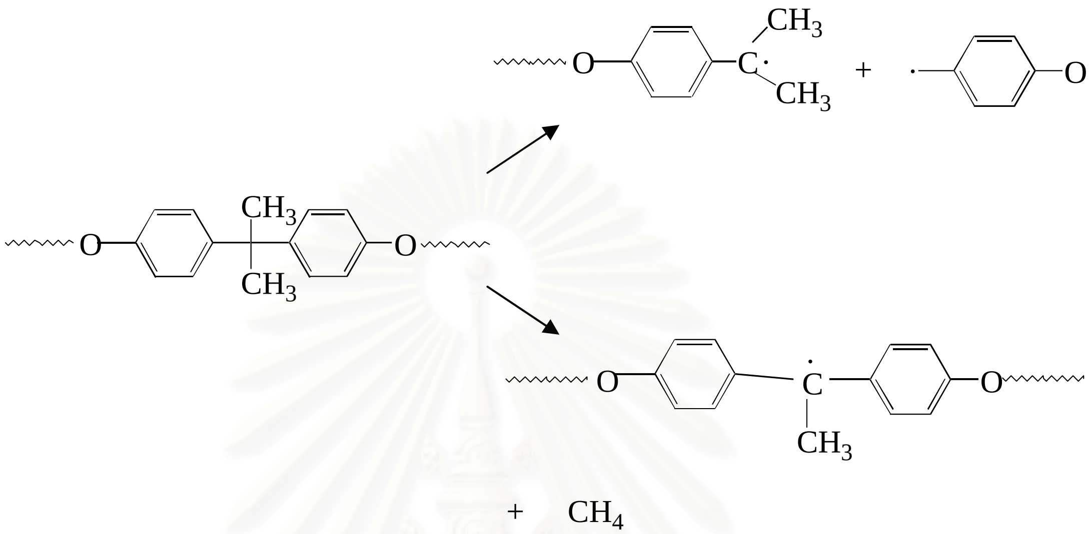


Figure 4.14 Isopropylidene cleavage in epoxy resin.

The FT-IR spectra of thermal degradation of phenolic resin are shown in Figure 4.15. These spectra are presented as a function of temperature. Phenolac novolac exhibited higher thermal stability, as compared to those with polybenzoxazine and cured epoxy resin. Several peaks remain in the spectrum of phenolic resin at 498 ^{o}C (i.e., hydroxyl group, aliphatic and aromatic hydrocarbon, and benzene ring). Therefore, phenolic novolac resin does not degrade completedly. Lee [14] proposed a homolytic cleavage of the methylene bridges, as Figure 4.16 (presented by dash line) by a chain scission path. After the cleavage step, the intermediate undergoes a hydrogen abstraction to produce the major phenolic resin compounds, phenol, cresol, and methylenebisphenol.

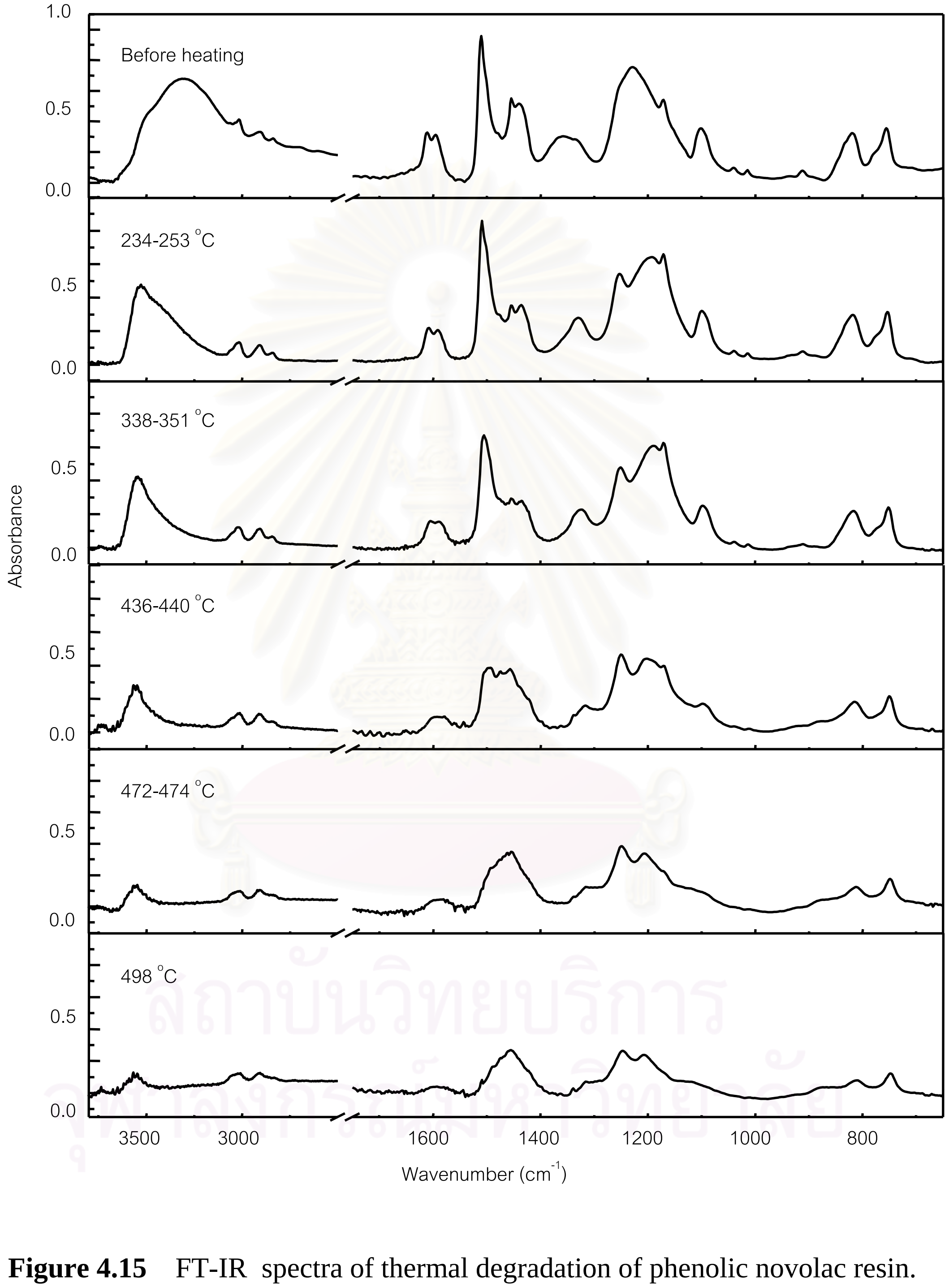


Figure 4.15 FT-IR spectra of thermal degradation of phenolic novolac resin.

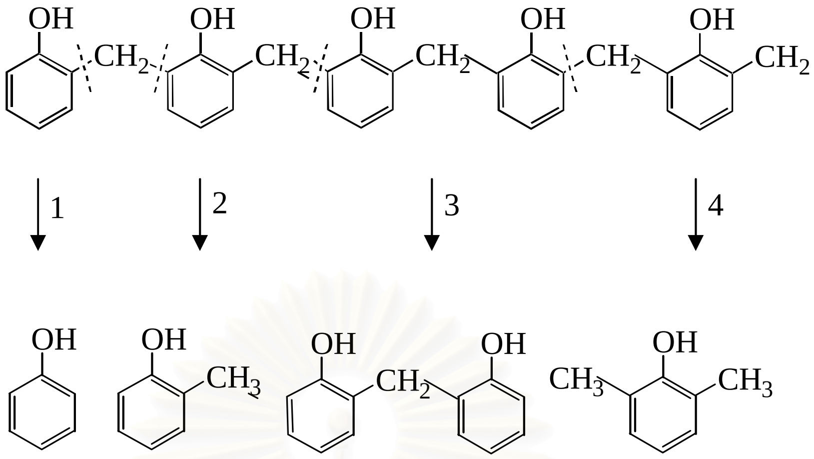


Figure 4.16 Degradation of phenolic novolac resin to produce phenol (1), cresol (2), methylenebisphenol (3), and dimethylphenol (4).

4.2. Thermal Degradation of Copolymers

In this research, BE21 and BP21 were represented as model compounds for studying degradation of copolymers of benzoxazine and epoxy resins, benzoxazine and phenolic resins, respectively. The chemical structure of copolymer of benzoxazine and epoxy resins is shown in Figure 4.17 with the FT-IR spectrum of cured BE21 is shown in Figure 4.18. The FT-IR band assignments of BE21 are shown in Table 4.5. The chemical structure of cured BP21 is shown in Figure 4.19. The FT-IR spectrum of cured BP21 in Figure 4.20. The FT-IR band assignment of cured BP21 is shown in Table 4.6.

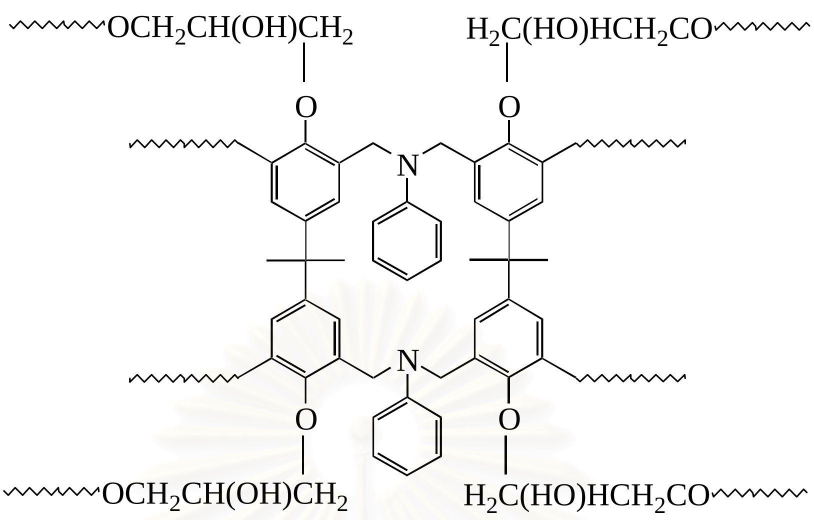


Figure 4.17 Chemical structure of copolymer of benzoxazine and epoxy resins.

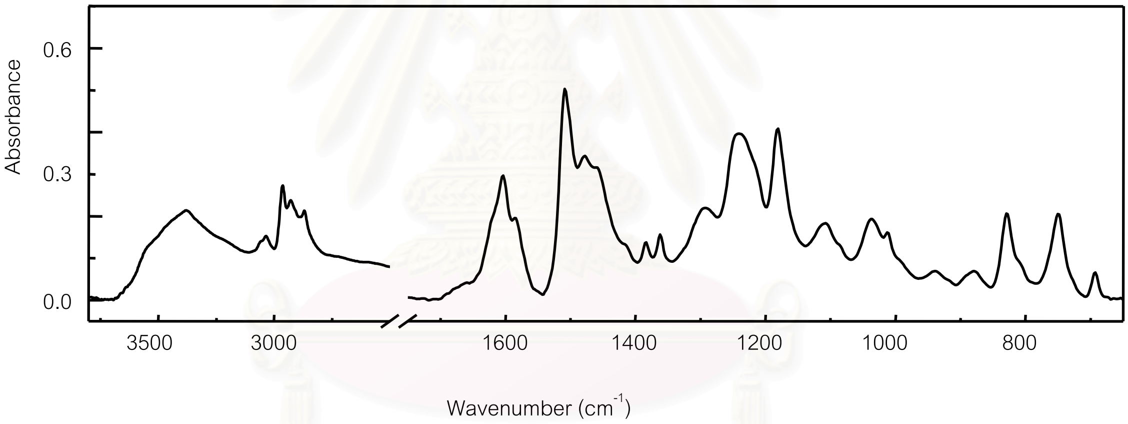


Figure 4.18 FT-IR spectrum of cured BE21.

Table 4.5 FT-IR band assignments of cured BE21

Peak position (cm^{-1})	Assignment
3390	O-H stretching of phenol
3040	C-H stretching of benzene ring
2971	C-H asymmetric stretching of methyl group
2924	C-H asymmetric stretching of methylene group
2874	C-H symmetric stretching of methylene group
1606, 1586, 1510, 1480	C=C stretching of benzene ring
1280	C-O(-C) symmetric stretching of epoxide ring
1242	C-N stretching of aromatic amine
1184	C-C stretching of Ar-C(-C)-Ar
1120	C-N stretching of aliphatic amine
1040	C-O stretching of alcohol
831	C-H out-of-plane vibration mode of deformation of 1,2,3,5-tetra-substituted benzene ring
757, 697	C-H out-of-plane vibration of five adjacent hydrogen atoms of mono-substituted benzene ring

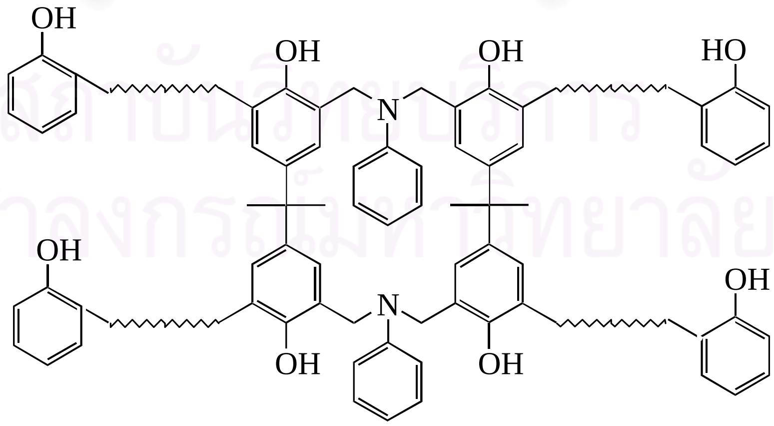


Figure 4.19 Chemical structure of copolymer of benzoxazine and phenolic resins.

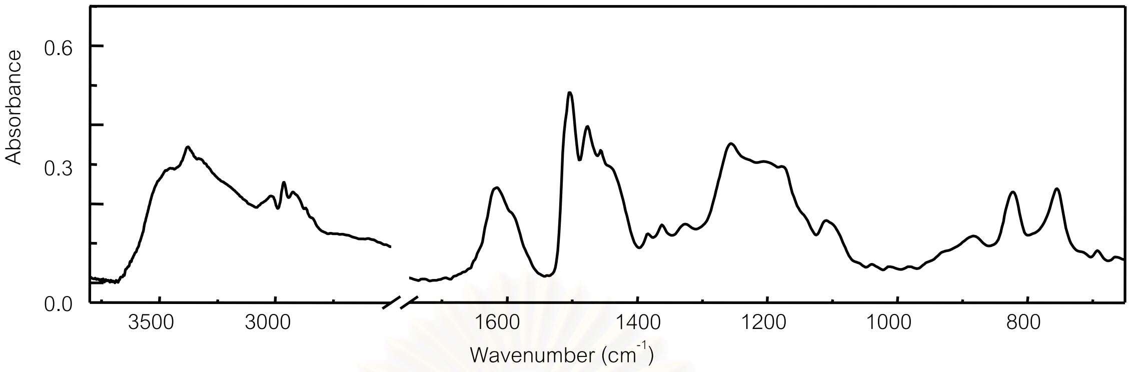


Figure 4.20 FT-IR spectrum of cured BP21.

Table 4.6 FT-IR band assignments of cured BP21

Peak position (cm^{-1})	Assignment
3456	O-H stretching of phenol (free hydrogen bond)
3379	O-H stretching of phenol (hydrogen bond)
3018	C-H stretching of benzene ring
2964	C-H asymmetric stretching of methyl group
2924	C-H asymmetric stretching of methylene group
2872	C-H symmetric stretching of methyl group
1671, 1505, 1477, 1456	C=C stretching of benzene ring
1256	C-N stretching of aromatic amine
1190	C-C stretching of Ar-C(-C)-Ar
1120	C-N stretching of aliphatic amine
885	C-H out of plane vibration mode of isolated hydrogen atom of 1,2,3,5-tetra-substituted of benzene ring
823	C-H out of plane vibration of five adjacent hydrogen atom of mono-substituted of benzene ring
757	C-H out of plane vibration of 1,2-di-substituted of benzene ring

4.2.1. TGA Analysis

The TGA thermogram of cured BE21 and cured BP21 are shown in Figure 4.21. Figure 4.22 shows derivative curve of cured BE21 and cured BP21. Table 4.7 represents thermal properties of cured BE21 and cured BP21, which is summarized from Figures 4.21 and 4.22. The temperature at 5% weight loss of cured BE21 is higher than those of polybenzoxazine and epoxy resin. Therefore, cured BE21 exhibits higher thermal stability. The temperature at 5% weight loss of cured BP21 is lower than the cured BE21. However, cured BP21exhibits higher char yield than cured BE21. This is due to the fact that both polybenzoxazine and phenolic novolac resin are known to give higher char yield comparing to the epoxy resin. Cured BE21 shows one major weight loss. Cured BP21, on the other hand, shows two major weight losses at 388 ^{o}C and 470 ^{o}C.

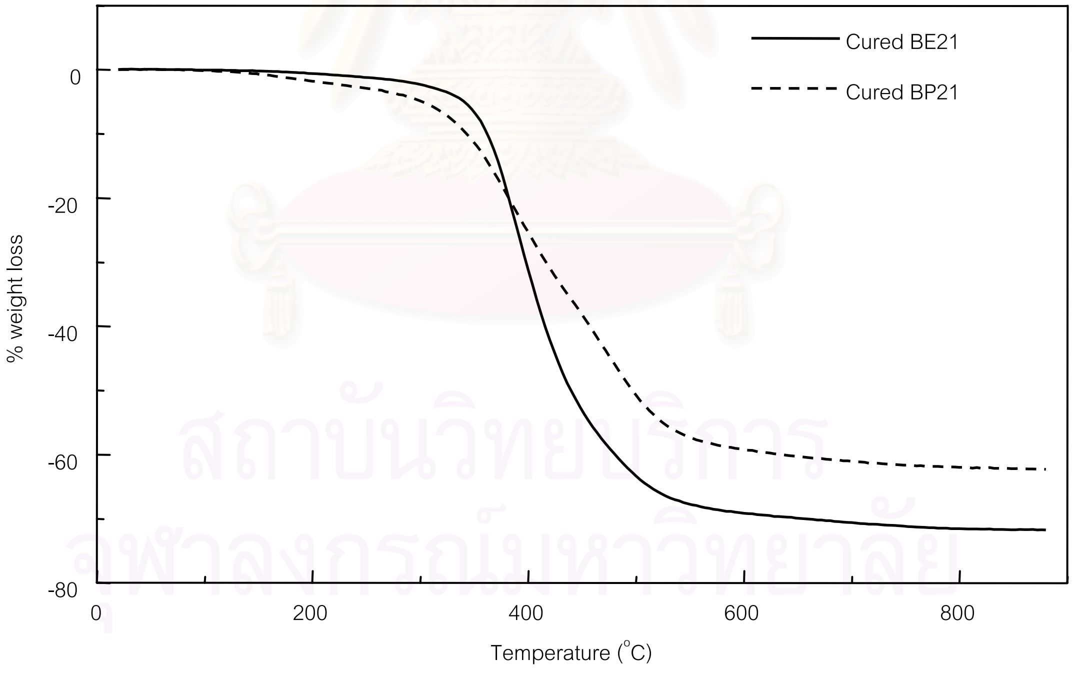


Figure 4.21 TGA thermograms observed with copolymer of benzoxazine and epoxy resins vs copolymer of benzoxazine and phenolic resins.

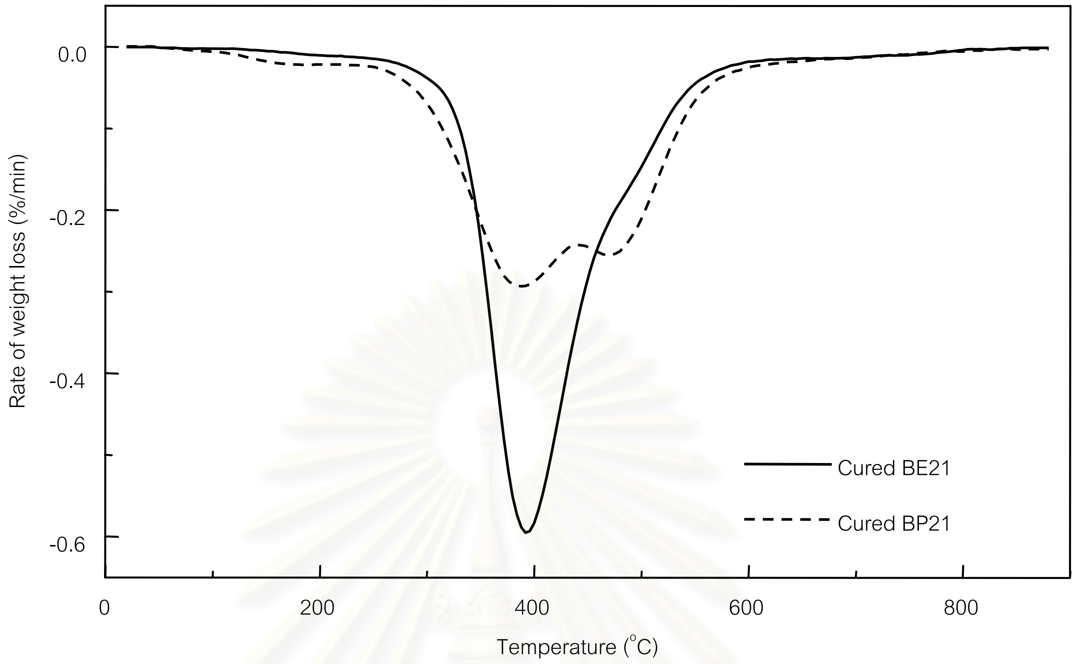


Figure 4.22 Derivatives of weight loss copolymer of benzoxazine and epoxy resins vs copolymer of benzoxazine and phenolic resins.

Table 4.7 Thermal properties of the copolymers

Condition	Cured BE21	Cured BP21
Temperature at 5% weight-loss (^{o}C)	340	302
Temperature at major peak (^{o}C)	388	388, 470
% residue at 800 ^{o}C	28.43	38.01

4.2.2. FT-IR Spectroscopy

Figure 4.23 shows the FT-IR spectra of thermal degradation of cured BE21. The band at 1282 cm^{-1} is assigned to the C-O stretching in epoxide ring. The intensity of this band decreases with increasing temperature until 367 ^{o}C where this band disappears. This is because epoxide rings in epoxy resin are opened by hydroxy group in benzoxazine. The band at 1120 cm^{-1} indicates the presence of C-N stretching vibration inside the Mannich base. In addition, The band intensity decreases with increasing temperature until 429 ^{o}C.

From TGA analysis of homopolymers, the decomposition temperature (temperature of 5% weight loss) of polybenzoxazine is lower than that of epoxy resin. As a consequence, the initial thermal degradation of cured BE21 occurs at Mannich base cleavage. The degradation mechanism for cured BE21 is proposed as in Figure 4.24.

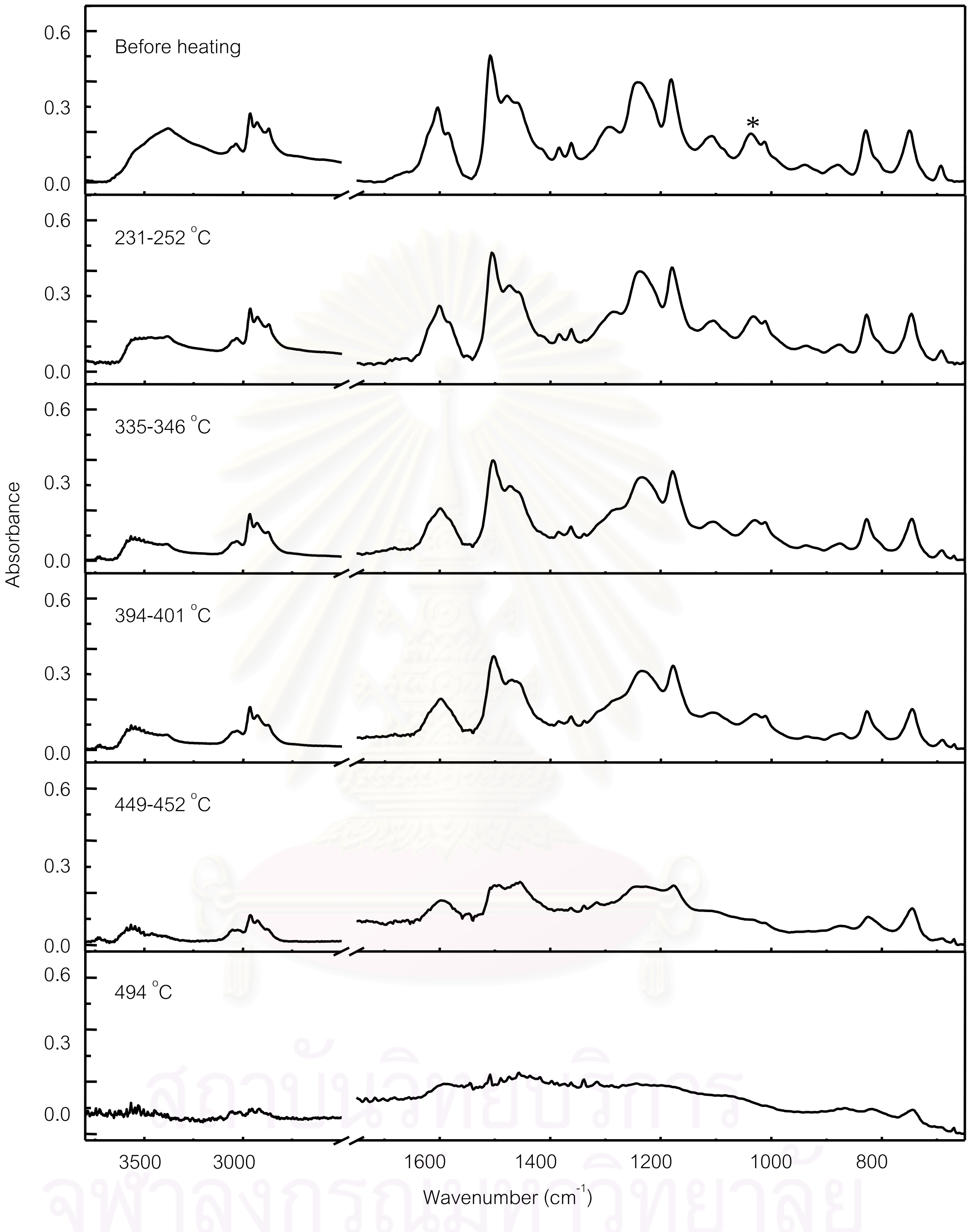


Figure 4.23 FT-IR spectra of thermal degradation of cured BE21

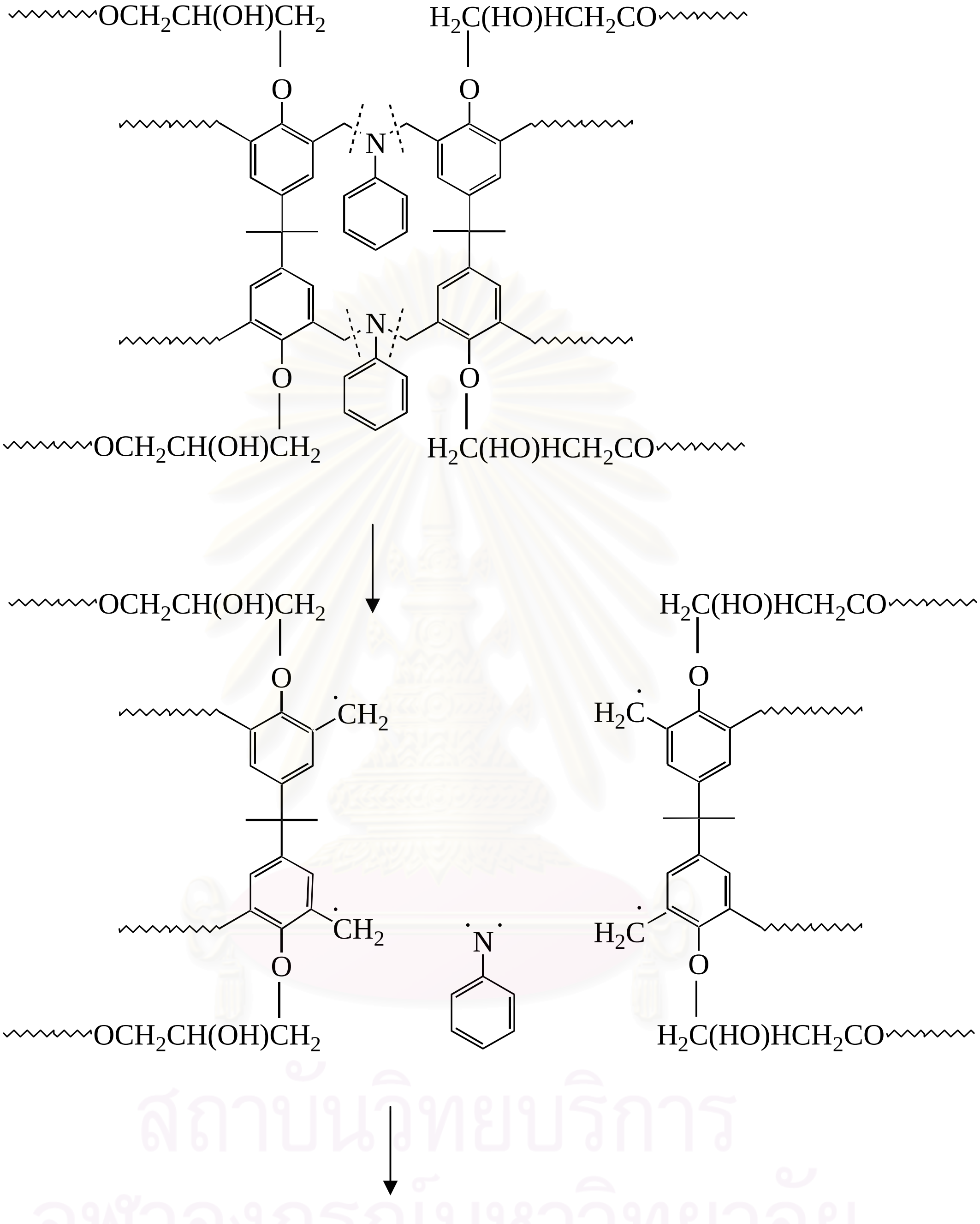


Figure 4.24 Proposed mechanism of Mannich base cleavage in copolymer of benzoxazine and epoxy resins.

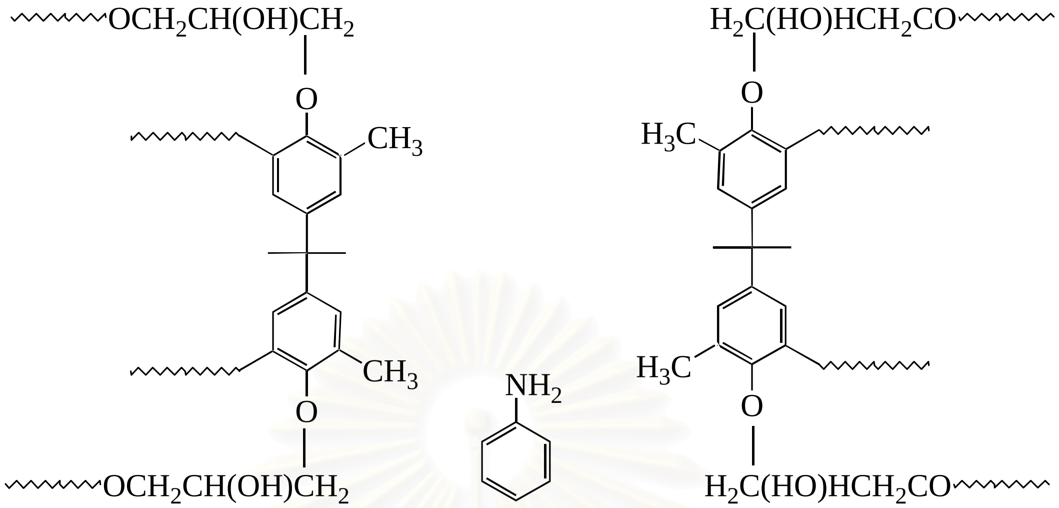


Figure 4.24 (continued) Proposed mechanism of Mannich base cleavage in copolymer of benzoxazine and epoxy resins.

Figure 4.25 shows the FT-IR spectra of thermal degradation of cured BP21. The band at 1120 cm^{-1} indicates the presence of C-N stretching vibration from Mannich base. The band intensity decreases with increasing temperature until reaching 441 ^{o}C. This band disappears faster than other peaks, thus cured BE21 or copolymer of benzoxazine and phenolic resin is degraded via thermal cleavage of Mannich base. End groups of copolymer of benzoxazine and phenolic resin are phenolic group, with polybenzoxazine in the center of the chain. Therefore, mechanism of Mannich base cleavage in copolymer of benzoxazine and phenolic resin is similar to that of polybenzoxazine (Figures 4.11 and 4.12).

This observation agrees very well with the results of TGA analysis. With TGA analysis, thermal degradation of cured BP21 occurs two mechanisms. Therefore, the first event is the Mannich base cleavage followed by the degradation of char, as seen on derivative curve in Figure 4.22, whose degradation product are phenolic resin and substituted benzene compound. The result is supported by those with FT-IR technique. FT-IR spectrum of thermal degradation for cured BP21 at 445 ^{o}C in Figure 4.25 shows aliphatic and aromatic hydrocarbons as well as substituted benzene compounds.

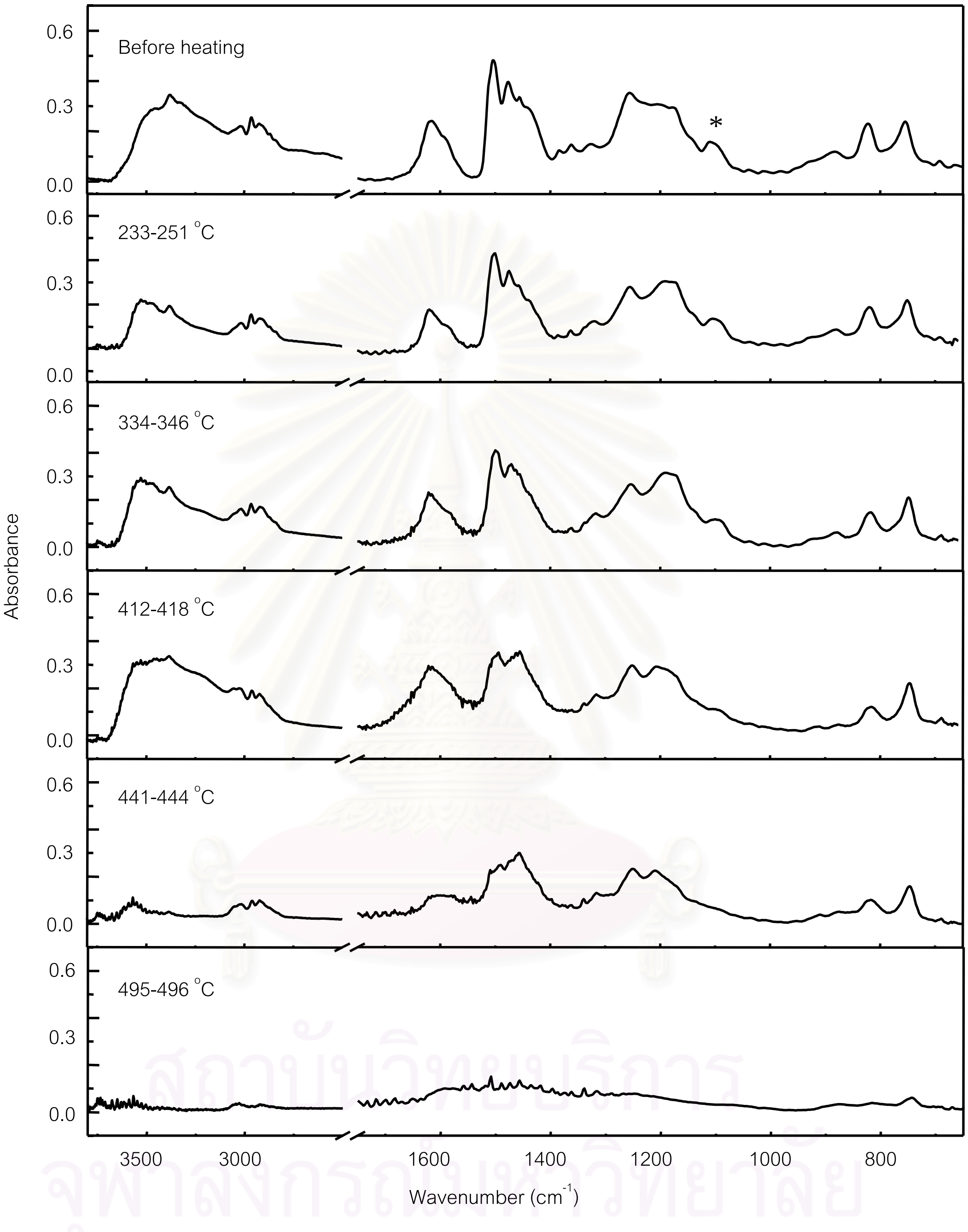


Figure 4.25 FT-IR spectra of thermal degradation of cured BP21.

4.3 Thermal Degradation of Terpolymer

The FT-IR spectrum of cured BEP514 is shown in Figure 4.26. The band assignments of cured BEP514 are shown in Table 4.8.

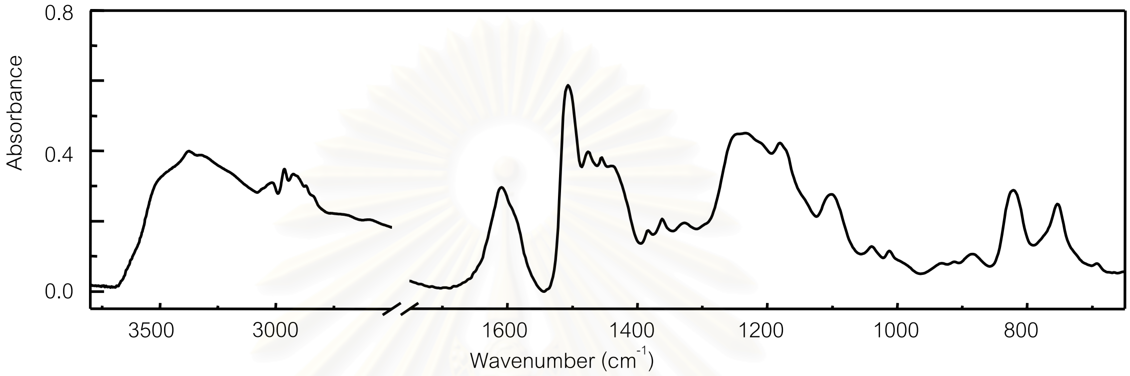


Figure 4.27 FT-IR spectrum of cured BEP514 resin.

Table 4.8 FT-IR band assignments of cured BEP514

Peak position (cm^{-1})	Assignment
3511	O-H stretching of phenol (free hydrogen bond)
3376	O-H stretching of phenol (hydrogen bond)
3018	C-H stretching of benzene ring
2964	C-H asymmetric stretching of methyl group
2923	C-H asymmetric stretching of methylene group
2873	C-H symmetric stretching of methyl group
1609, 1505, 1476, 1452	C=C stretching of benzene ring
1385	C-H symmetric deformation of geminated methyl group of bisphenol A
1238	C-O(-Ar) asymmetric stretching of aliphatic aromatic ether
1182	C-C stretching of Ar-C(-C)-Ar
1110	C-N stretching of aliphatic amine
885	C-H out-of-plane vibration mode of isolated hydrogen atom of 1,2,3,5-tetra-substituted benzene ring
825	C-H out-of-plane vibration of five adjacent hydrogen atoms of mono-substituted benzene ring
757	C-H out-of-plane vibration of 1,2-di-substituted benzene ring

4.3.1 TGA Analysis

The TGA thermogram of cured BEP514 is shown in Figure 4.27. The derivative curve of cured BEP514 is shown in Figure 4.28. Table 4.9 shows thermal properties of cured BEP514. The cured BEP514 exhibits two major weight-losses representing two mechanisms for thermal degradation of cured BEP514 at 380 and 480 °C.

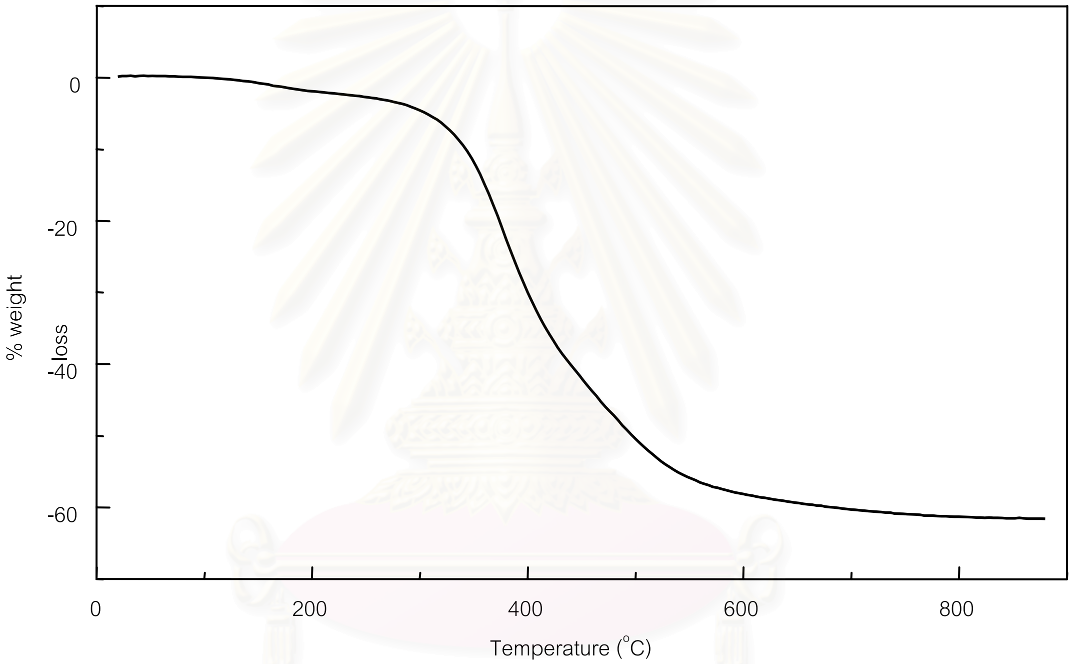


Figure 4.27 TGA thermogram of cured BEP514.

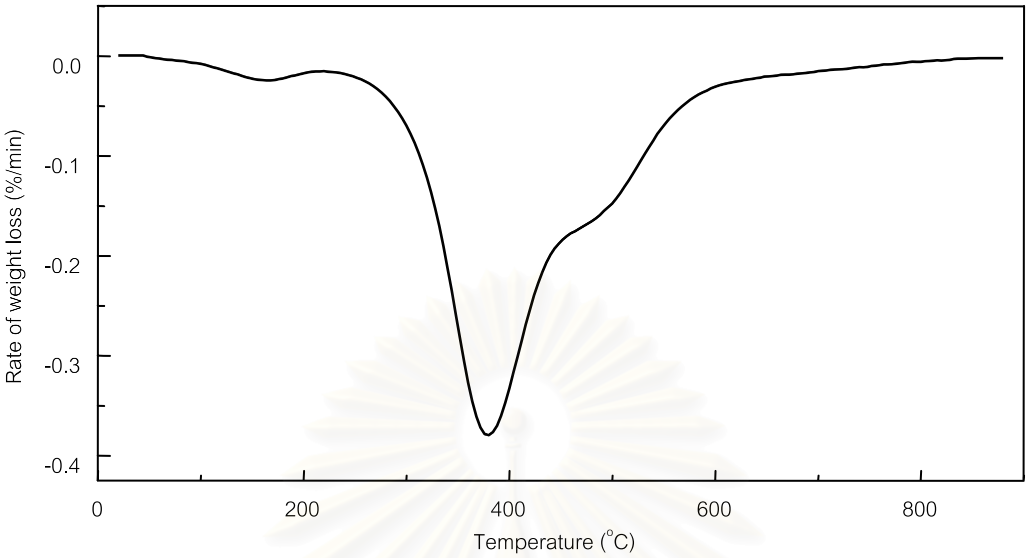


Figure 4.28 Derivative of weight loss for cured BEP514.

Table 4.9 Thermal properties of cured BEP514

Conditions	BEP 514
Temperature at 5% weight loss (°C)	307
Temperature at major peak (°C)	380, 480
% residue at 800 °C	38.7

4.3.2 FT-IR Analysis

Figure 4.29 shows FT-IR spectral series of thermal degradation of cured BEP514. Upon heating the sample, the C-N stretching peak from Mannich base at 1115 cm^{-1} decreases before others do. This suggests that the cured BEP514 is degraded by thermal cleavage of Mannich base. The proposed thermal cleavage of Mannich base from the terpolymer of benzoxazine, epoxy resin, and phenolic resin is shown in Figure 4.30. The observation agrees very well with TGA analysis which present the first event from derivative curve of cured BEP514 (Figure 4.28) where the Mannich base cleavage occurs.

According to Figure 4.29, FT-IR spectrum of cured BEP514 shows some significant peaks (i.e., aliphatic and aromatic hydrocarbon peak, benzene ring, and substituted benzene ring peak) at 498 °C. Therefore, the latter event is the degradation of char, whose degradation products are phenolic resin and substituted benzene compounds.

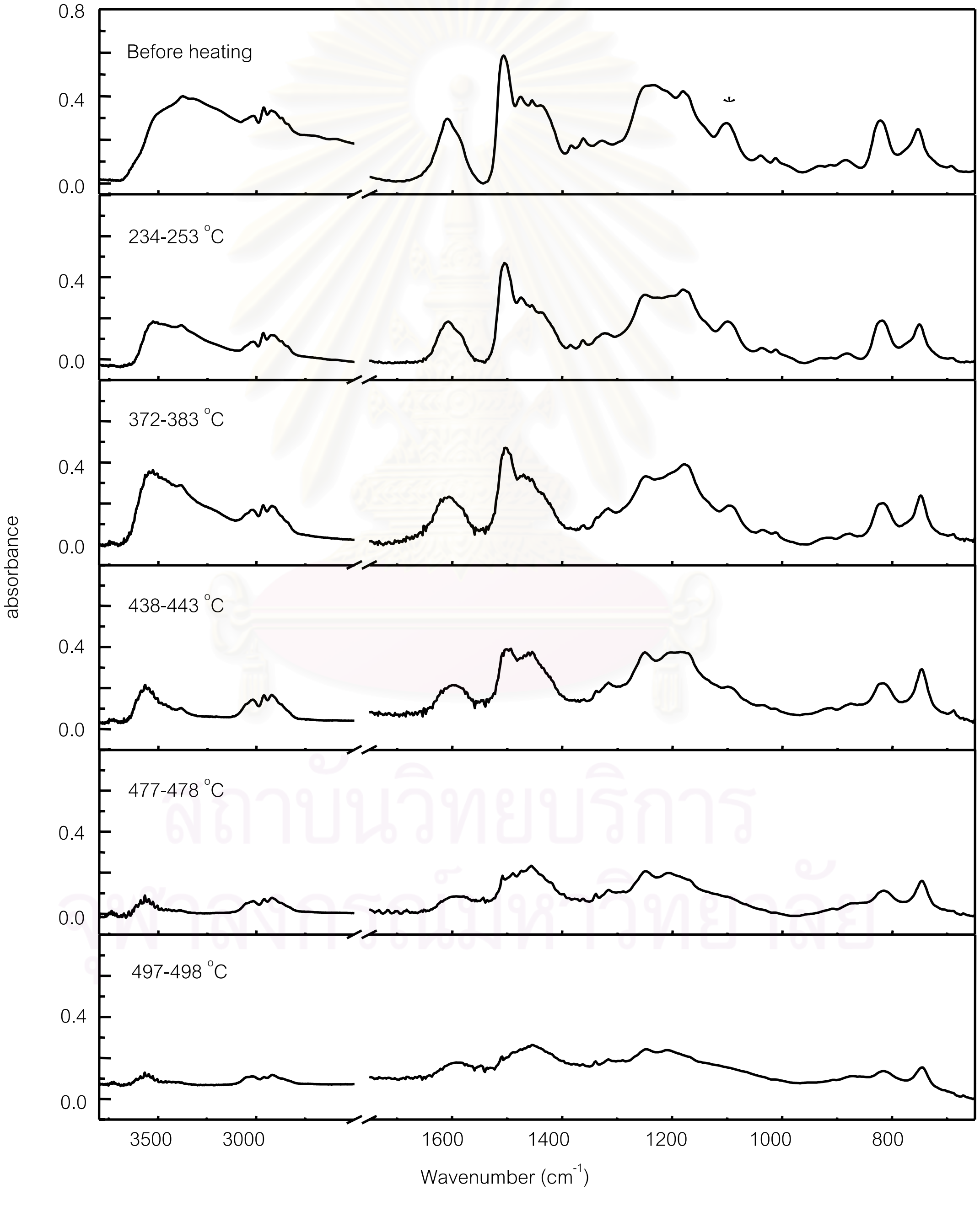


Figure 4.29 FT-IR spectra of thermal degradation of cured BEP514.

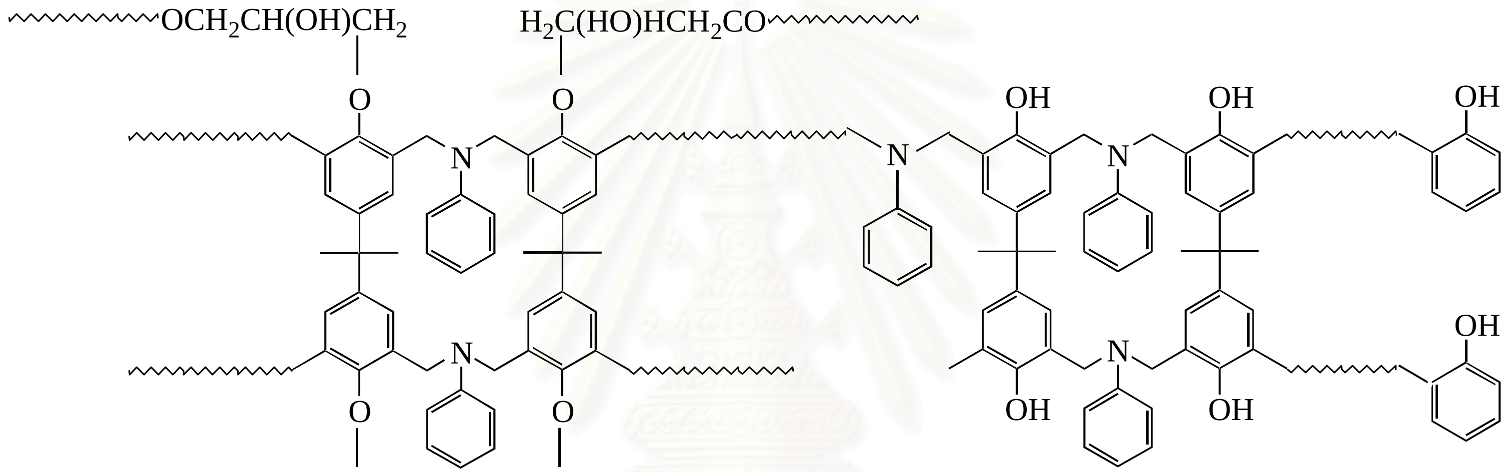


Figure 4.30 Proposed structure for terpolymer of benzoxazine, epoxy, and phenolic resins

Figures 4.31, 4.32, and 4.33 show the FT-IR spectra with time at 300 ^{o}C, 330 ^{o}C, and 360 ^{o}C, respectively. Cured BEP514 exhibited high thermal stability due to the spectrum of each heating temperature showed many peaks after heated for 180 minutes. At the temperature of 300 ^{o}C and 330 ^{o}C, C-N stretching appeared until 180 minutes, while at 360 ^{o}C it disappeared after 150 minutes.

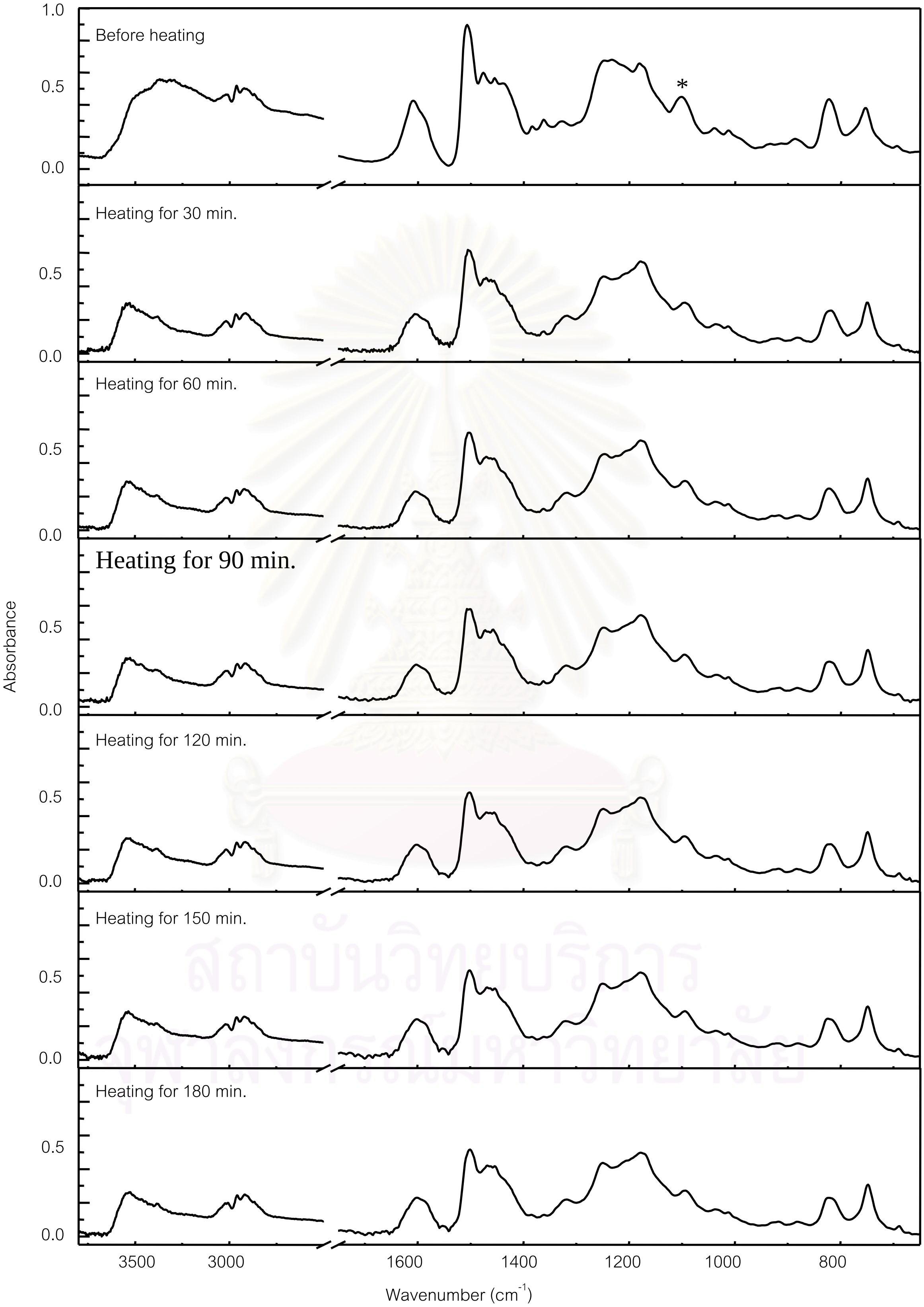


Figure 4.31 FT-IR spectra of cured BEP514 at 300 °C with different heating times

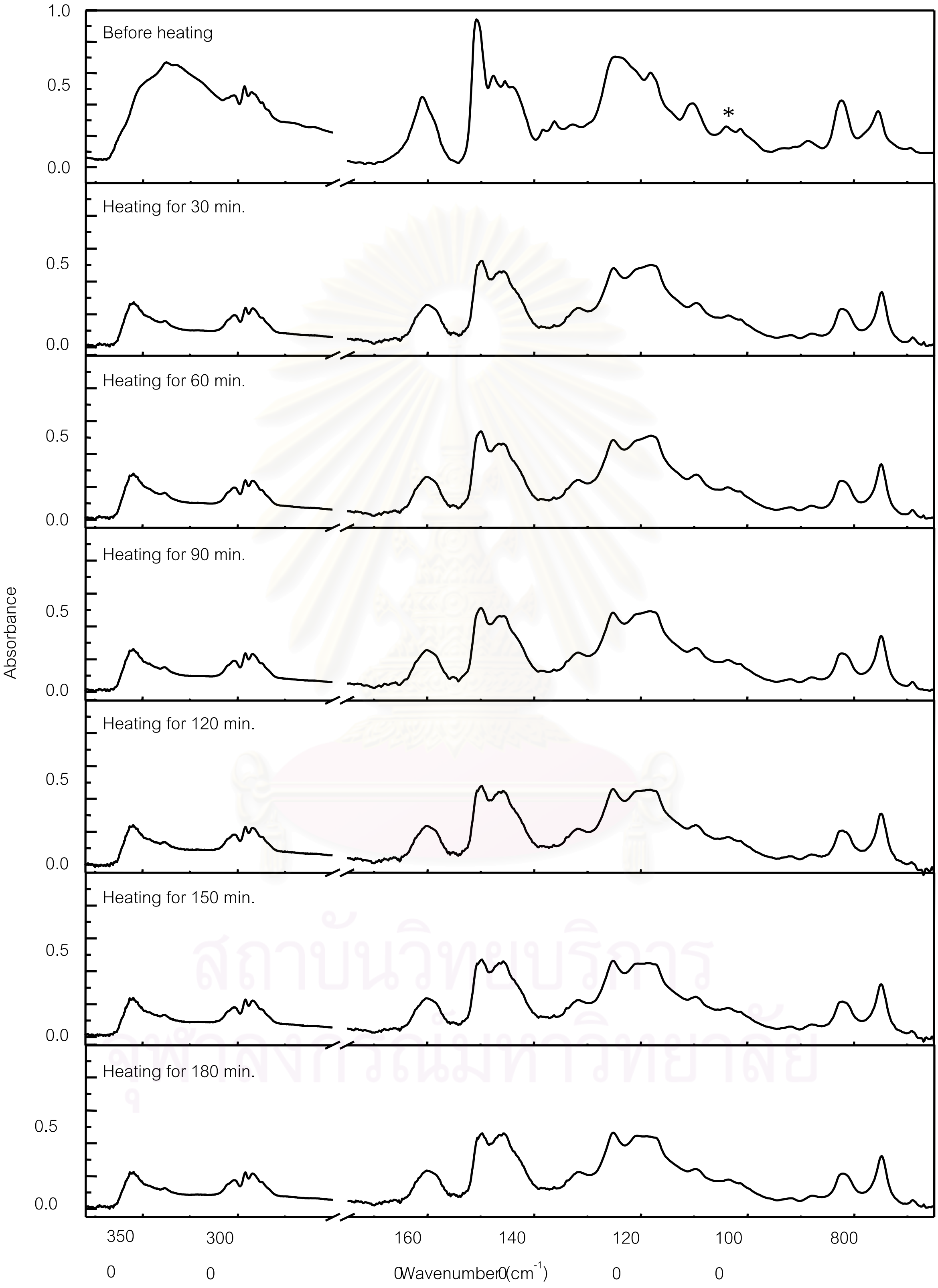


Figure 4.32 FT-IR spectra of cured BEP514 at 330 °C with different heating times

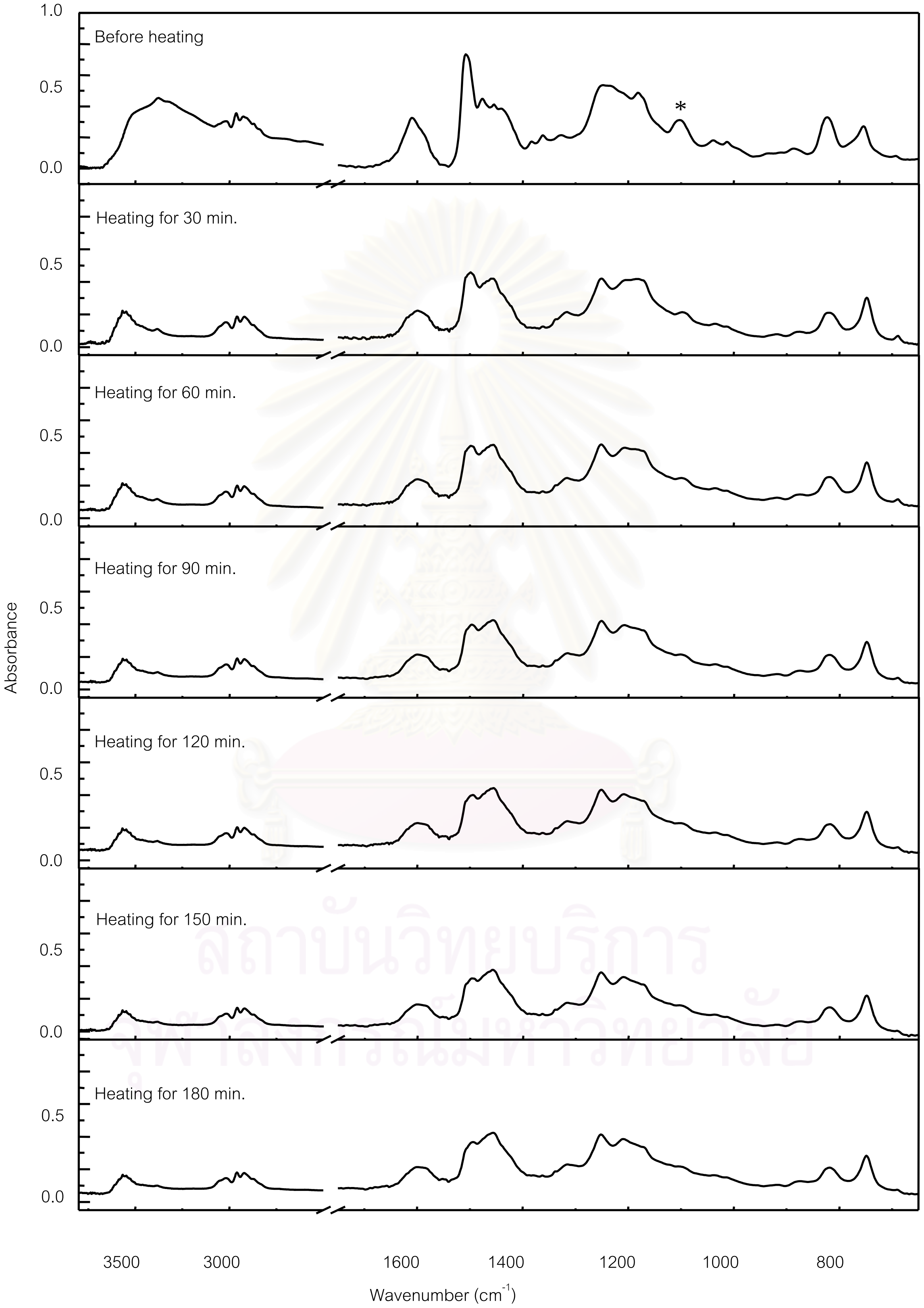


Figure 4.33 FT-IR spectra of cured BEP514 at 360 ^{o}C with different heating times

CHAPTER 5

CONCLUSIONS

The thermal degradation of terpolymer based on ternary system of benzoxazine, epoxy, and phenolic resins has been investigated. Thermogravimetric analysis (TGA) has been employed for determining thermal stability of the terpolymer while Fourier transform infrared (FT-IR) spectroscopy is utilized for observing the structural change during the degradation process. Before investigation of thermal degradation of the terpolymer, the following systems were studied for comparison, homopolymers of polybenzoxazine, epoxy resin, and phenolic resin; copolymer of benozoxazine and epoxy resins and copolymer of benzoxazine and phenolic resins.

Polybenzoxazine is less thermally stable than the epoxy homopolymer due to the labile Mannich base. The degradation products are aniline and various types of phenols. For epoxy polymer, isopropylidene bond dissociation occurs during initial thermal degradation.

The copolymer based on benzoxazine and epoxy resins shows a mechanism for thermal degradation by Mannich base cleavage. The thermal degradation of the copolymer of benzoxazine and phenolic resins, on the other hand, shows two major mechanisms. The first mechanism is the Mannich base cleavage. The second one, which takes place at higher temperature, is the degradation of char, which produces phenol derivatives and substituted benzene compounds.

The mechanism for thermal degradation of the terpolymer is similar to that of the copolymer of benzoxazine and phenolic resins. The Mannich base degraded first for the terpolymer followed by the degradation of char at a higher temperature.

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APPENDIX

APPENDIX

Picture of instrument and accessories used in this research.

(a) (b)

Hot Cell (a) and Temperature Controller (b)

VITAE

Miss Nopparat Thaweewthananon was born in Chonburi, Thailand, on November 12th, 1978. She received Bachelor Degree of Science in 1999 from Department of Industrial Chemistry, Faculty of Applied Science, King Mongkut's Institute of Technology North Bangkok. She started as a Master-Degree student with a major in Polymer Science, Petrochemical and Polymer Science Program, Chulalongkorn University in 1999 and complete the program in 2002.