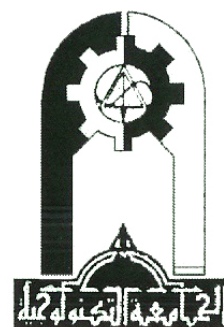


**Ministry of Higher Education
& Scientific Research
University of Technology
Chemical Engineering Department**



RHEOLOGICAL AND KINETIC STUDY OF DIGLYCIDYL ETHER OF BISPHENOL-A (DGEBA) CURED WITH PHENYLENEDIAMINE

A THESIS

**Submitted to the Chemical Engineering Department of the University
of Technology in Partial Fulfillment of the Requirements for the
Degree of Master of Science in Chemical Engineering/Unit Operation**

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September

2011

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

(شَهِدَ اللَّهُ أَنَّهُ لَا إِلَهَ إِلَّا هُوَ وَالْمَلَائِكَةُ وَأُولُوا
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صدق الله العظيم

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A decorative border with a repeating floral and leaf pattern in black and white, framing the entire page.

My family for their continued
support

Thanks

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ABSTRACT

The cure process of epoxy resin diglycidyl ether of bisphenol-A (DGEBA) with aromatic amine (m-PDA) was studied by means of differential scanning calorimetry (DSC) Perkin Elmer Pyris 6, and Brookfield RV-II viscometer. Isothermal DSC measurements were conducted between 80 and 110 °C, at 10 °C intervals. The results show that the maximum cure reaction was achieved at 110 °C. The maximum degree of cure at isothermal cure temperature 110 °C was 0.9. The isothermal cure process was simulated with Kamal modifier with diffusion model, the model agrees well with the experimental data. The glass transition temperature was also studied by DSC of each curing temperature, and the final glass transition temperature $T_{g\infty}$ increase with increasing of degree of cure was observed. The maximum temperature achieved was (117 °C.) at curing temperature 110 °C.

The dynamic cure process was different from the isothermal cure process. For dynamic cure process, the activation energy was determined by two methods. One was based on Kissinger and Ozawa approach, given only one activation energy for the whole curing process. There was a slightly difference between the obtained activation energy and pre-exponential factor, 63.6 and 70.7 kJ mol⁻¹ respectively. Another method was based on isoconversional, given activation energy at any conversion, and observed the E_a decrease with increment conversion (67-63) KJ/mol.

Rheological properties of epoxy resin system are closely related to the cure process. With the development of the cure reaction, gelation occurs and

ABSTRACT

epoxy system becomes difficult to process. It was found that the isothermal temperature increases, the gel time decreases. The activation energy was calculated by Arrhenius law. Viscosity profiles were described by Sun model. The fitted results agreed well with the experimental values. The critical time in the model decreases with increasing of the isothermal temperature. The activation energies determined by the gel time, and critical time are close to each other 79.07 and 79.46 kJ mol⁻¹ respectively. The gel time obtained by DSC measurement different from those obtained from rheological measurement.

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CHAPTER ONE

INTRODUCTION

Epoxy resins represent an important class of polymers primarily due to their versatility. High degree of crosslinking and the nature of the interchain bonds give cured epoxies many desirable characteristics. These characteristics include excellent adhesion to many substrates, high strength (tensile, compressive and flexural), chemical resistance, fatigue resistance, corrosion resistance and electrical resistance⁽¹⁾. In addition, processing is simplified by the low shrinkage and lack of volatile by-products. Properties of the uncured epoxy resins, such as viscosity, which are important in processing,⁽²⁾ as well as final properties of cured epoxies such as mechanical strength or electrical resistance can be optimized by appropriate selection of the epoxy monomer and the curing agent or catalyst.⁽³⁻⁴⁾ Because of the ease of application,⁽⁵⁾ and desirable properties, epoxies are widely used for coatings,⁽⁶⁻⁷⁾ corrosion protectants,⁽⁸⁾ electronic encapsulate,⁽⁹⁾ fiber optic sheathing,⁽¹⁰⁾ flooring and adhesives, in fiber-reinforced composite,⁽¹¹⁾. The market for epoxy resins has grown as new epoxies are developed and new applications are found,⁽¹²⁻¹³⁾. Two important advantages of these resins: first, they can be partially cured and stored in that state, and second they exhibit low shrinkage during cure epoxy resins can be cured with either catalytic or co-reactive curing agents. A catalytic curing agent functions as an initiator for epoxy resin homopolymerization, whereas the co-reactive curing agent acts as comonomer in the polymerization process,⁽¹⁴⁾. In order to optimize the curing cycles for epoxy resin, it is necessary to understand the cure kinetics. Differential scanning calorimetry or DSC is one of the methods used

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to analyze the cure kinetics,⁽¹⁵⁾. This is done by integrating the peak corresponding to a given transition⁽¹⁶⁾. Multi kinetic models are available to analysis curing kinetic one from models is n^{th} order reaction. This model gave a good fit to the experimental data only in a limited range of degree of cure⁽¹⁷⁾. Another model can be used to describe curing kinetic with more complexity is autocatalytic model⁽¹⁸⁾.

Some of the rheological properties such as viscosity change during cure processes therefore rheological analysis is important because it has been used to study the cure process of epoxy resin ⁽¹⁹⁾. Viscoelastic characteristics change, which is reflected in the variations of the viscosity η , the gel point can be calculated from the change in viscosity, the gel point represents the onset of formation of networking ⁽²⁰⁾.

1.2 Objectives

The objectives of the research are as follows:

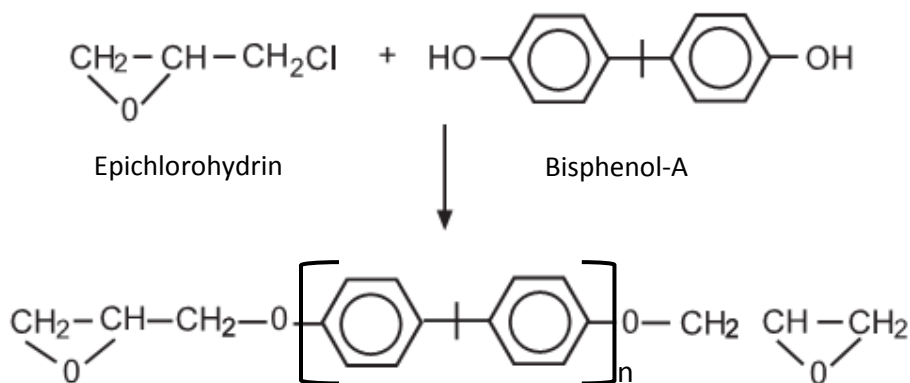
1. To determine curing kinetics by measuring heat flow of DGEBA/m-PDA system under isothermal and non- isothermal condition.
2. To measure the rheological properties such as the viscosity from which a gel time is determined.
3. To determine $T_{g\infty}$ from the DSC measurement
4. Comparison of kinetic and rheological evaluation of gel time for DGEBA/m-PDA system.
5. To compare with the existing kinetic and viscosity models and show the agreement or disagreement.

CHAPTER TWO

LITERATURE SURVEY

2.1 Epoxy Resins

Epoxy resin is defined as a molecule containing more than one epoxide groups. The epoxide groups also termed as, oxirane or ethoxyline group, these resins are thermosetting polymers and are used as adhesives, high performance coatings, potting and encapsulating materials. These resins have excellent electrical properties, low shrinkage, good adhesion to many metals and resistance to moisture, thermal and mechanical shock. There are two main categories of epoxy resins, namely the glycidyl epoxy, and non-glycidyl epoxy resins. The glycidyl epoxies are further classified as glycidyl-ether, glycidyl-ester and glycidyl-amine. The non-glycidyl epoxies are either aliphatic or cycloaliphatic epoxy resins. Glycidyl epoxies are prepared via a condensation reaction of appropriate dihydroxy compound, dibasic acid or a diamine and epichlorohydrin. While, non-glycidyl epoxies are formed by peroxidation of olefinic double bond. Glycidyl-ether epoxies such as, diglycidyl ether of bisphenol-A (DGEBA) and novolac epoxy resins are most commonly used epoxies ⁽²¹⁾. The first liquid diepoxide as the reaction product of bisphenol-A with an excess of epichlorohydrin. (Scheme 1). This resin is commonly called, diglycidylether of bisphenol A



Scheme 1: Diglycidylether of Bisphenol-A (DGEBA)⁽¹⁴⁾

(DGEBA). The general-purpose resins prepared by the reaction of bisphenol - A and epichlorohydrin in the presence of strong base were first marketed in the 1940s. The molecular weight of the resin depends on the feed ratio of epichlorohydrin/bisphenol-A and an increase in this ratio results in a decrease in molecular weight. The development of high molecular weight solid epoxy resins by using (i) direct reaction of bisphenol-A with epichlorohydrin and caustic using appropriate ratios to form a resinous mass along with salt and water (known as the “taffy process”) and (ii) using a liquid diepoxide resin as a starting material for reaction with bisphenol-A thereby eliminating the need for removal of salt and water (fusion technique)⁽¹⁴⁾. These resins are

characterized by epoxy equivalent weight (EEW), the presence of glycidyl units in these resins enhances the processability⁽²¹⁾.

2.2 Curing Agents

Epoxy has the ability to transform its readily liquid (or thermoplastic) state to tough, hard thermoset solids. This hardening is accomplished by the addition of a chemically active reagent known as a curing agent⁽²²⁾. Optimum performance properties can be obtained by cross-linking the epoxy resins into a three-dimensional and infusible network. The choice of curing agent depends on processing method, curing conditions, i.e., curing temperature, time, physical, chemical properties desired, toxicological, environmental limitations, and cost. The epoxy group, because of its three-membered ring structure, is highly reactive and can be opened up by a variety of nucleophilic and electrophilic reagents, curing agents are either catalytic or coreactive. Catalytic curing agents, including Lewis bases, Lewis acids and photoinitiated cationic cures; function as initiators for epoxy resin homopolymerization. Coreactive curing agents, including amines and acid anhydride, act as comonomers in the polymerization process⁽¹⁴⁾.

2.2.1 Aliphatic amines.

These curing agents gel rapidly at room temperature, but a complete through cure at room temperature will take about five to seven days. Heating the material can reduce this time to a few hours. A higher temperature is not recommended since some of these curing agents contain plasticizers intended to remain in the thermosets and they may volatilize

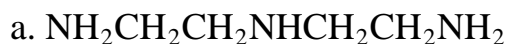
during the cure. Diethylenetriamine (DETA) and triethylenetetramine (TETA) are highly reactive aliphatic amines.

2.2.2 Cycloaliphatic amines.

These curing agents gel rapidly at room temperature but a complete cure at room temperature is not possible. Heating the material is necessary for optimum properties. 1, 2-Diaminocyclohexane (DACH) is one from cycloaliphatic amines compounds.

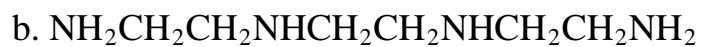
2.2.3 Aromatic amines.

These curing agents gel very slowly at room temperature, but like cycloaliphatic amines a complete cure at room temperature is not possible. Curing at high temperature initially is not recommended in general, characteristics such as stiffness, strength, and glass transition temperature increase with increased crosslink, but toughness decreases⁽²³⁾. m-phenylenediamine (m-PDA) are principal commercial aromatic amines. Among the aromatic amines, m-phenylenediamine (m-PDA) provides the highest cross-link density and exhibits best solvent resistance, (Scheme 2)⁽²⁴⁾

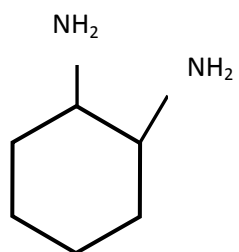


Diethylenetriamine (DETA)

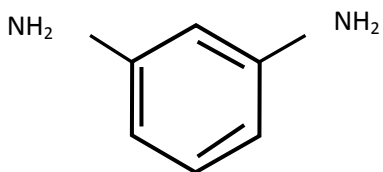
LITERATURE SURVEY



Triethylenetetramine(TETA)



c.1, 2-Diaminocyclohexane (DACH)



d.meta-phenylenediamine (m-PDA)

Scheme 2: (a, b) Aliphatic amines, (c) Cycloaliphatic amines, (d) Aromatic amines⁽²⁴⁾.

2.3 Curing Kineticsof Epoxy-Amine System

Curing kinetics of epoxy resin with amines has been extensively investigated over the past four decades. Their physical, mechanical and electrical properties depend to a large extent on the degree of cure. On the other hand, their processability depends on the rate and extent of reaction under process conditions. The knowledge of mechanism and curing kinetics is not only important for a better understanding of the structure property relations, but it is also fundamental in optimizing process conditions and product qualities.

2.3.1 Chemistry

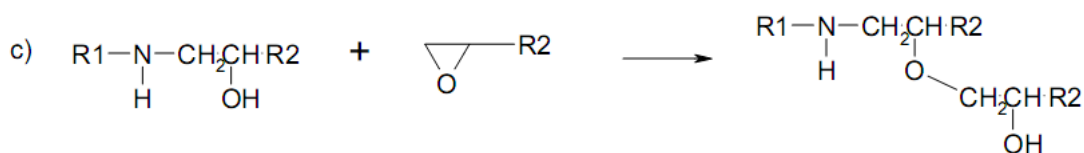
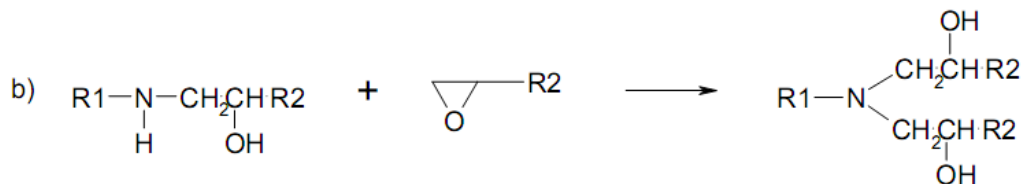
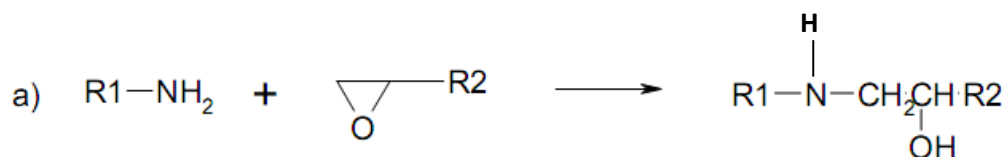
The ring-opening polymerization and crosslinking in epoxy resins can be of two general types,

1. Catalyzed homopolymerization
2. Bridging reactions which incorporate a coreactive crosslinking agent into the network.

Homopolymerization, or reactions between epoxy chains, involve elimination reactions on the oxygen atom of the epoxide group using acid or base catalysts⁽²⁵⁾. The incorporation, or bridging reaction, involves nucleophilic attack on one of the epoxide carbons by an amine or an anhydride compound⁽²⁶⁻²⁷⁾. An obvious and important difference in the result of the two different curing methods is that in homopolymerization the network is only composed of the cross-linked epoxy monomers, whereas in the bridging reaction the network is composed of a copolymer of both epoxy monomers and a curing agent, as shown in Scheme 3. Therefore in a bridging reaction the network properties are a function of two components, which allows modifications to be incorporated in either component. Thus, a rigid

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epoxy with high strength can be used with an impact resistant hardener to yield a desirable network⁽²⁸⁾. In addition, in amine-cured epoxy reactions a side reaction between the products and reactants occurs, as shown in Scheme 3c. Epoxy monomers may be attacked by the hydroxyl group of the product of the primary amine opened epoxy⁽²⁹⁾.



Scheme 3: Mechanism of primary amine cure of an epoxy resin, with the epoxide group under nucleophilic attack by a) a primary amine, b) a Secondary amine and c) a hydroxyl group generated from reactions a and b.

2.3.2 Curing

Epoxy curing involves two phenomena, polymerization and crosslinking. Although each phenomenon is complicated and the two are in competition during the overall curing process, generalizations and simplified models can be made. During the initial stage of curing, polymerization is favored,⁽³⁰⁾ because in the case of catalyzed homopolymerization, terminal epoxides are the most reactive, and in the case of coreactive agents, primary reactions are more reactive than secondary ones. Also, the terminal epoxide reactivity already mentioned plays a role. In most cases the polymerization is an addition reaction⁽³¹⁾. The molecular weight of the growing polymer increases until the molecular weight approaches infinity, so that all monomers are connected by at least one bond and a network is formed⁽³²⁾. This point is called the gel point,⁽³³⁾ the polymer possesses high molecular weight and few crosslinks, and thus behaves much like a very high molecular weight thermoplastic⁽³⁴⁾. From the gel point, crosslinking becomes the dominant phenomenon due to the lack of free monomers. Crosslinking involves interchain bonding of intrachain reactive sites, either intrachain epoxides or secondary sites on coreactive agents⁽³⁵⁾. Although crosslinking is a different phenomenon, the rate of chemical

conversion of the epoxide groups is unaffected in most epoxy systems⁽³⁶⁾. The crosslinking reactions produce a growing network and reduce the mobility of the chain segments. The growth of the network results in mechanical and thermal stabilization of the structure, resulting in increasing modulus,⁽³⁷⁾ and glass transition and degradation temperatures⁽³⁸⁾. At a certain high degree of crosslinking, the increasing molecular weight of the structure exceeds the molecular weight which is thermodynamically stable as a rubber, and the material transforms into a glass, a process called vitrification⁽³⁹⁾. In a glassy state, the mobility of reactants is severely restricted, reducing the rate of the reaction to a diffusion-controlled reaction, which is much slower. Further conversion is still possible; however, the rate is much slower since the process relies on diffusion rather than mobility to bring the reactants together. When the crosslinking reaction exhausts all the reactive sites available, the resulting structure is hard (high modulus) and insoluble due to a high degree of interchain bonding⁽⁴⁰⁾.

2.4 Heat of Reaction

Due to the high potential energy of the ring-strained epoxide groups in the uncured resin, there is a large Gibbs function difference associated with the ring-opening reaction. Since the Gibbs function change is expressed in the form of both enthalpic (ΔH) and entropic (ΔS) changes, the reaction is called exergonic⁽⁴¹⁾. Although structural changes will result in a significant entropy change, the enthalpy change is the dominant product. The change in enthalpy results in the evolution of thermal energy or heat, making this an exothermic reaction. Since the opening of the epoxide rings have much higher energy (and enthalpy) differences than the other reactions,

the amount of heat evolved and the rate of evolution will correspond to the number of epoxide groups reacting and the rate of the reaction. Reactions which generate heat are studied by calorimetry⁽⁴²⁾.

2.5 The Mixing Ratio or Stoichiometric Ratios

The relationship between reactive groups in a reaction is important. Because unreacted groups can lead to different properties⁽⁴³⁾. The mixing ratio or stoichiometry between curing agents and resins has a great effect on the physical and the mechanical properties of the epoxy resin⁽⁴⁴⁾.

2.5.1 Calculation of Stoichiometric Ratios

To obtain optimum properties with polyfunctional epoxide-reactive curing agents, it is desirable to react the resin and the curing agent at approximately stoichiometric quantities. To determine the ratio required, calculations can be made as follows:

1. To calculate the Amine H equivalent weight, the following equation can be used:

Equation (1):

$$\text{Amine H eq wt} = \frac{\text{Mwt of amine}}{\text{no. of active hydrogen}} \quad (2.1)$$

2. To calculate the stoichiometric ratio:

Equation (2):

$$phr\ of\ amine = \frac{Amine\ H\ eq\ wt \times 100}{Epoxide\ eq\ wt\ of\ resin} \quad (2.2)$$

Where phr is parts by wt per 100 parts resin ⁽⁴⁵⁾.

2.6 Determine cure kinetic

Various experimental techniques have been developed for cure reactions of thermosets. These techniques include chromatography, infrared spectroscopy, nuclear magnetic resonance, dielectric spectroscopy, raman spectroscopy, calorimetry, chemical analysis and dynamic mechanical measurement, etc. Generally differential scanning calorimetry (DSC) has been mostly used for the estimation of kinetic parameters. This calorimetric technique gives a quantitative measurement on the heat of reaction and permits the determination of the glass transition T_g of materials. The DSC technique was used to investigate the kinetics of the epoxy system. However, it should be noted that the complementary nature of several techniques, including IR spectroscopy, chromatography, and rheological measurements, can provide such information. By DSC, two basic approaches are used to determine the curing kinetics—the isothermal approach, where a single curve temperature is used at a given cure cycle, and the dynamic approach, where the rate of heat is kept constant for a given cure cycle. Kinetic parameters were determined from dynamic and isothermal DSC data with the assumption that the exothermic heat

evolved during cure is proportional to the extent of monomer conversion⁽⁴⁶⁾.

2.7. Kinetic Models and Equation

Chemical kinetics is the description of conversion of reactants to products. The traditional chemical method for kinetic rate determination is mechanistic - the concentrations of products or reactants are monitored throughout the reaction and the rates of change in concentrations are fitted to an equation. Once the mechanism is determined and modeled, then the reaction can be described by reactant or product concentrations in time as a function of a temperature dependant rate constant⁽⁴⁷⁾. However, many curing reactions are quite complex, involving multiple competing reactions with several kinetic equations superimposed at different degrees during the overall reaction, producing very complicated models⁽⁴⁸⁻⁴⁹⁾. In addition, in

many instances the exact chemistry or concentrations of reactants may not be known, especially in industrial applications where premixed compounds or prepreg composites are supplied by an outside source. For these situations, phenomenological models are attractive and have demonstrated value and validity⁽⁵⁰⁻⁵²⁾. Phenomenological models use properties which are related to the reaction, for example the change in viscosity or shift in glass transition temperature of a growing polymer. These models describe the degree of conversion or percent of cure from uncured to fully cure as a function of time and temperature. Phenomenological models are advantageous because they do not require knowledge of the reaction mechanism, only the changes in properties.

2.7.1 Kinetic Equations

As any chemical reaction, the curing reaction will be described by a rate equation, which will relate the rate of the reaction to the rate constant and the consumption of reactants or production of products. In the case of thermoset curing, a generalized rate function utilizing the degree of cure, α , which is the disappearance of epoxide functional groups or appearance of chemical bonds, with $(1 - \alpha)$ representing the epoxide group concentration.

$$d\alpha/dt = k (1 - \alpha)^n \quad (2.3)$$

This equation describes an nth order equation, so that the reaction rate is dependant only on the concentration of epoxide (and curing agent). However, many thermosetting materials are autocatalytic, so that the product of the reaction serves as an additional catalyst in the reaction, as in the catalyzation of the epoxy-amine system by generated hydroxyl groups. Kinetic modeling of autocatalytic reactions requires an additional term to account for this effect, namely

$$d\alpha/dt = k \alpha^m (1 - \alpha)^n \quad (2.4)$$

where α^m represents the catalytic effect of the products of the reaction with an order of m. It is also apparent, that an nth order reaction is a special case of the autocatalytic reaction where $m = 0$.

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However, the two types are readily differentiated by experimental data. As can be easily predicted from Equation 2.3, an n th order reaction will exhibit its maximum rate at the beginning of the reaction, whereas the autocatalytic reaction, predicted from Equation 2.4, will exhibit its maximum rate at some later time during the reaction, typically 20 to 40 % of the reaction ⁽⁵³⁾. In addition to the time dependence of the rate of conversion, the rate constant, k , is temperature dependent, usually assumed to follow an Arrhenius relation of the form:

$$k = A \exp(-E_a/RT) \quad (2.5)$$

Where k is the reaction rate constant, A is the pre-exponential function, and E_a is the activation energy. Thus, Equations 2.3 and 2.4 can be written as

$$d\alpha/dt = (Ae^{-E_a/RT}) (1 - \alpha)^n \quad (2.6)$$

$$d\alpha/dt = (Ae^{-E_a/RT}) \alpha^m (1 - \alpha)^n \quad (2.7)$$

With the incorporation of the Arrhenius temperature dependence. The initial rate of an autocatalytic reaction is not necessarily zero since the reaction can proceed via alternative paths, especially in the presence of impurities like water and catalyzing ions.

Taking this into account, the autocatalytic equation is given as

$$d\alpha/dt = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (2.8)$$

Where k_1 is the reaction rate constant at zero time and k_2 is the rate constant of the reaction by traditional pathways. The initial rate constant, k_1 , is easily calculated from the experimental data since it equals the rate at zero conversion. Both m and n are the kinetic exponents of the reaction, and $m+n$ is the overall reaction order. Both kinetic constants, k_1 and k_2 depend on temperature according to Arrhenius law. Such a model has been successfully applied to describe the initial stage of cure of epoxy/diamine systems. Kamal showed that the model was valid only for the initial stage of cure but not for the later stage of cure where the reaction mechanism was diffusion controlled. Kamal with diffusion model can be defined as⁽⁵⁴⁾

$$\frac{d\alpha}{dt} = \frac{1}{1+\exp(C(\alpha-\alpha_c))} (K_1 + K_2\alpha^m)(1 - \alpha)^n \quad (2.9)$$

where m , n , k_1 , and k_2 are the same as those of the autocatalytic equation. The term $1/(1+\exp(C(\alpha-\alpha_c)))$ is the diffusion factor that includes two constants: C , the diffusion constant, and α_c , the critical degree of cure. A , ΔE , C , m , and n are the parameters of the model found by fitting the curve to the da/dt vs. α and T data.

Lee et al.⁽⁵⁵⁾ proposed a model for more complex reactions. The model was separated into two elemental parts. One was represented by the

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nth order type of reaction and the other was by the autocatalyzed type of reaction, shown as:

$$\frac{d\alpha}{dt} = K_a(1 - \alpha)^l + K_b\alpha^m(1 - \alpha)^n \quad (2.10)$$

where k_a and k_b are the non-catalyzed and autocatalyzed rate constant, respectively, and l, m, n are the respective reaction orders.

Cole⁽⁵⁶⁾ proposed a model with diffusion factor. It can be defined as

$$\frac{d\alpha}{dt} = \frac{1}{1 + \exp\left(C(\alpha - (\alpha_{c0} + \alpha_{cT}T))\right)} (K\alpha^m)(1 - \alpha)^n \quad (2.11)$$

where m and n are the first and second exponential constants, respectively, and k is the rate constant. The term $1/(1 + \exp(C(\alpha - (\alpha_{c0} + \alpha_{cT}T))))$ is the diffusion factor that includes three constants: C , the diffusion constant; and α_0 , the critical degree of cure at $T = 0K$; and α_T , a constant that accounts for increase in the critical resin degree of cure with temperature. A , ΔE , C , α_0 , and α_T are the parameters of the model found by fitting the curve to the $d\alpha/dt$ vs. α and T data.

2.7.2 Kinetic Methods

2.7.2.1 Isothermal Differential Scanning Calorimetry

In this method an uncured sample is cured isothermally in a calorimeter at desired curing temperatures for a certain period of time. This

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method allows monitoring of the conversion and the rate of conversion simultaneously over the entire course of reaction. The heat of cure at time t , ΔH_t , can be measured directly from the partial area under the isothermal curve. The degree of curing at time t , α_t can be defined as

$$\alpha_t = \Delta H_t / \Delta H_{\text{tot}} \quad (2.12)$$

where ΔH_{tot} is the total heat liberated when a completely uncured resin is taken to complete cure. Thus, the reaction rate or rate of conversion, $d\alpha/dt$ is:

$$\frac{d\alpha}{dt} = \frac{dH}{dt} \frac{1}{\Delta H_{\text{tot}}} \quad (2.13)$$

where dH/dt or heat flow represents the rate of heat generated during curing reaction.

2.7.2.2 Multiple Scanning Rates DSC

This method provides the kinetic parameters with accuracy. It is valuable as a precursor to isothermal studies and is often the only means to analyze the curing kinetics of system with multiple exotherms⁽⁵³⁾. A basic concept of the analysis is that the peak exotherm temperature T_p varies in a predictable manner with heating rate β . According to the Kissinger method⁽⁵⁷⁾, the activation energy can be obtained from the maximum reaction rate where the exothermal peak appears under a constant heating rate.

$$\ln\left(\frac{\beta_i}{T_{p,i}^2}\right) = \ln(AR/E_a) - E_a/RT_{p,i} \quad (2.14)$$

Thus, the activation energy E_a can be obtained from the slope of the plot of $\ln\left(\frac{\beta}{T_p^2}\right)$ as a function of $1/T_p$ without a specific assumption of the conversion-dependent function.

Ozawa ⁽⁵⁸⁾ developed an alternative method to determine the activation energy from T_p . The equation shows as following:

$$\ln(\beta_i) = Const. - 1.052 E_a/RT_{p,i} \quad (2.15)$$

Thus, E_a can be obtained from the slope of the plot of $\ln\beta$ as a function of $1/T_p$.

Another method for determining E_a was first developed by Fava⁽⁵⁹⁾, named as an isoconversional method. The isoconversional method allows complex processes to be detected by a variation of E_a with α . This method is based on the assumption that the reaction rate at a constant conversion depends only on the temperature. Based on this concept⁽⁶⁰⁻⁶¹⁾, the equation for determining the activation energy is given by:

$$\ln(\beta_i) = Const. - 1.052 E_a/RT_{\alpha,i} \quad (2.16)$$

Where $T_{\alpha,i}$ is the temperature at different conversions at different heating rates.

2.7.3 Physical Models

2.7.3.1 Glass Transition Temperature

During the polymerization part of the reaction, before gelation and crosslinking, the increase in Tg associated with the linear chain growth is proportional to the concentration of monomers, using the decrease in concentration in the form

$$1/Tg = 1/Tg_0 + k\alpha \quad (2.17)$$

where Tg_0 is the glass transition temperature at zero conversion, k is the rate constant and α is the conversion, which is only valid for values up to gelation. This equation assumes that no crosslinking takes place, which is a good approximation at low conversion.

In the region between gelation and vitrification where crosslinking is the dominant reaction, two primary models have been used. Fox and Loshaek⁽⁶²⁾ proposed a model which predicts a linear increase in Tg with crosslink density, whereas DiMarzio⁽⁶³⁾ proposed a model which predicts linearity of $1/Tg$ with crosslink density. Later modeling approaches combined effects, polymerization and crosslinking, into one model. The

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first of these, T_g as a function of conversion models was proposed by DiBenedetto.

DiBenedetto⁽⁶⁴⁾ established a relationship to predict the shift in T_g based on lattice energies and segmental mobilities of the cured and uncured materials,

$$\frac{T_g - T_{g0}}{T_{g0}} = \frac{(\varepsilon_{\infty} / \varepsilon_0 - C_{\infty} / C_0) x}{1 - (1 - C_{\infty} / C_0) x} \quad (2.18)$$

where x is the crosslink density or fraction of segments crosslinked, ε is the lattice energy, and C is the segmental mobility. This equation has been used successfully for many cross-linking systems. This equation was modified by Couchman⁽⁶⁵⁾ to combine the lattice energy and segmental mobility into the heat capacity value,

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda \alpha}{1 - (1 - \lambda) \alpha} \quad (2.19)$$

This equation was found to model some systems with λ values ranging from between 0.46 and 0.58.⁽⁶⁶⁾ However, the equation does not adequately model epoxy-rich systems, due to the complexity of the reactions⁽⁴⁸⁻⁴⁹⁾. Venditti and Gillham⁽⁶⁷⁾ further modified the equation to the following form:

$$\ln(T_g) = \frac{(1 - \alpha) \ln(T_{g0}) (\Delta C_{p\infty} / \Delta C_{p0}) \alpha \ln(T_{g\infty})}{(1 - \alpha) + (\Delta C_{p\infty} / \Delta C_{p0}) \alpha} \quad (2.20)$$

This equation was found to model the epoxy-rich systems, which the previous models could not, in addition to the systems which were modeled by the other equations.

2.7.3.2 Rheology

Rheology is the study of the flow and deformation of matter. It describes the relationship between force, deformation and time, the term comes from the Greek "rheos" that means to flow. The consistency of different products describes fluid rheology. Fluid rheology is studied by viscosity and elasticity. Viscosity is the resistance to flow and elasticity is usually stickiness or it is the property whereby a solid material changes its shape under opposing forces and tends to recover its shape when the force is removed⁽⁶⁸⁾.

2.7.3.2.1 Viscosity Model

Viscosity of the thermosetting resins changes drastically during cure. The resin viscosity depends on the cure temperature and degree of cure. As such, advanced viscosity models should include these two variables. Viscosity models are often fitted to the complex viscosity data obtained during cure of the thermosetting resins and composites using the rheometer.

1. Ampudia Model

The Ampudia viscosity model relates the complex viscosity of the thermosetting resin with its isothermal cure time and is defined as⁽⁶⁹⁾

$$\eta^* = \eta_1 \exp(k't) \quad (2.21)$$

where η^* is the complex viscosity, t is the isothermal cure time, and η_1 and k' are defined by the following equations:

$$\eta_1 = \eta_a \exp\left(\frac{E_\eta}{RT}\right) \quad (2.22)$$

$$k' = k'_\infty \exp\left(-\frac{E_k}{RT}\right) \quad (2.23)$$

where η_a and k'_∞ are constants, E_η and E_k are the activation energies, R is the universal gas constant, and T is the absolute isothermal cure temperature. Parameters η_a , k'_∞ , E_η , and E_k of the model are found by fitting the curve to the η^* vs. t data.

2. Dusi Model

The Dusi viscosity model, which has found the most application in complex viscosity modeling for thermosetting resins, is defined as⁽⁷⁰⁾

$$\eta^* = \eta_a \exp(k'\alpha) \exp\left(\frac{U}{RT}\right) \quad (2.24)$$

where η^* is the complex viscosity, η_a is a constant, α is the degree of cure, U is the activation energy for viscosity assumed to be independent of the degree of cure, k' is a constant assumed to be independent of temperature, R is the universal gas constant, and T is the absolute temperature. Parameters η_a , k' , and U of the model are found by fitting the curve to the η^* vs. α and T

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data. To make the curve fitting easier, one can take the natural log of both sides of the above equation to obtain the following:

$$\ln \eta^* = \ln \eta_a + k' \alpha + \frac{U}{RT} \quad (2.25)$$

3. Kenny Model

The Kenny viscosity model is defined as⁽⁷¹⁾

$$\eta^* = A_\mu \exp(E_\mu / RT) \left[\frac{\alpha_g}{\alpha_g - \alpha} \right]^{A_1 + B_1 \alpha} \quad (2.26)$$

where η^* is the complex viscosity, α is the degree of cure, α_g is the degree of cure at gelation, R is the universal gas constant, T is the absolute temperature, E_μ is the activation energy, and A_μ , A_1 , and B_1 are constants. Parameters A_μ , A , B , and E_μ of the model are found by fitting the curve to the η^* vs. α and T data. To make the cure fitting easier, equation (2.26) is rewritten in the natural log form as

$$\ln \eta^* = \ln A_\mu + \frac{E_\mu}{RT} + (A_1 + B_1 \alpha) \ln \left(\frac{\alpha_g}{\alpha_g - \alpha} \right) \quad (2.27)$$

4. SunModel

The Sun viscosity model is developed for the isothermal cure of epoxy preregs and is defined as⁽⁷²⁾

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$$\eta^* = \frac{\eta_0 - \eta_\infty}{1 + \exp[-k'(t - t_c)]} + \eta_\infty \quad (2.28)$$

Where η^* is the complex viscosity, η_0 and η_∞ are the initial and final complex viscosities during isothermal cure, respectively, t is the isothermal cure time, k' is a rate constant, and t_c is the critical time defined by

$$t_c = A_t \exp(E_t/RT) \quad (2.29)$$

where A_t is the pre-exponential factor, E_t is the activation energy, R is the universal gas constant, and T is the absolute temperature. Parameters η_0 and η_∞ are directly found from the complex viscosity data. Parameters A_t and E_t of the model are found by fitting the curve to the η^* vs. T data.

5. Stolin model

The Stolin viscosity model is defined as ⁽⁷³⁾

$$\eta = \eta_\infty \exp(E_\eta/RT) - K\alpha \quad (2.30)$$

where η_∞ is the viscosity at maximum cure, α is a constant, E_η is the activation energy of the viscosity change, and K is a constant.

2.7.3.2.2 Gelation and Gel Time Model

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Gelation refers to the point during the curing reaction where the molecular weight approaches the maximum, usually assumed to be infinite, meaning that all monomers are connected to the network by at least one chemical bond. While gelation is a microscopic effect, it produces macroscopic effects. Microscopic gelation refers to the definition of the gelation phenomenon, i.e. all monomers connected by at least one bond to the network. Since it occurs at a defined point in polymerization, it will occur at a specific degree of conversion. Microscopic gelation is difficult to measure⁽⁷⁴⁾.

The degree of conversion at the microscopic gel point can be calculated if the chemistry of the reactants is known. The first formula for calculating the microscopic gel point, proposed by Flory⁽⁷⁵⁾ in 1941, is

$$(\alpha_1 \alpha_2)_{gel} = \frac{1}{(f_1-1)(f_2-1)} \quad (2.31)$$

where α_1 is the conversion of reactant 1, α_2 is the conversion of reactant 2, f_1 is the functionality of reactant 1, f_2 is the functionality of reactant 2, and

$$\alpha_2 = B \alpha_1 \quad (2.32)$$

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where B is the stoichiometric ratio. For an epoxy-amine reaction, where the amine is reactant 1 and the epoxy is reactant 2, B is the ratio of amino hydrogens to epoxide groups, so equation (2.31) reduces to

$$\alpha_{2gel} = \left(\frac{B}{(f_1-1)(f_2-1)} \right)^{1/2} \quad (2.33)$$

Gel time, which was detected by the rheological measurement, varies with the isothermal cure rate of reaction.

Gonis et al.⁽⁷⁶⁾ expressed the curing process as:

$$\frac{d\alpha}{dt} = k(T) g(\alpha) \quad (2.34)$$

where $k(T)$ is the rate constant (which depends on the temperature T), and $g(\alpha)$ is a function of α only. It may have different forms, depending on the cure mechanism. The rate constant $k(T)$ has the same definition as in equation (2.5). By integrating the equation (2.34) from zero time to gel time t_{gel} , the relationship between t_{gel} and cure rate is obtained:

$$t_{gel} = \frac{1}{k(T)} \cdot \int_0^{\alpha_{gel}} \frac{1}{g(\alpha)} d\alpha \quad (2.35)$$

where α_{gel} is the degree of cure at gel time.

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Substituting equation (2.5) into equation (2.35) and taking logarithm on both sides to obtain the relationship between the gel time and isothermal cure temperature:

$$\ln(t_{gel}) = \ln\left[\frac{1}{A_0} \left\langle \int_0^{\alpha_{gel}} \frac{1}{\alpha_{gel}} d\alpha \right\rangle\right] + \frac{E_a}{R} \cdot \frac{1}{T} \quad (2.36)$$

By considering the first term on the left side of equation (2.36) as a constant C , a linear relationship of $\ln(t_{gel})$ vs. $1/T$ is obtained and equation (2.36) can be rewritten as:

$$\ln(t_{gel}) = C + \frac{E_a}{R} \cdot \frac{1}{T} \quad (2.37)$$

From equation (2.37), the apparent activation energy can be calculated from the slope of the curve of $\ln(t_{gel})$ vs. $1/T$.

2.8 Review of previous work

2.8.1 Review on the kinetic

Shechter et. al⁽⁷⁷⁾ studied the cure mechanisms of epoxy-amine systems. He found that a hydroxyl group only served as a catalyst for the reactions and

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was not a serious contender in competition with amines. The reaction rates of primary and secondary hydrogens with epoxide occur almost simultaneously, and only one overall reaction can be detected—this has been manifested by a single DSC peak.

Horie et. al.⁽¹⁸⁾ studied the reaction between phenyl glycidyl ether and n-butyl amine in the presence of n-butyl alcohol. He found that the uncatalyzed reaction behaved according to the third order autocatalytic kinetics, but the second order kinetics was observed in the reaction catalyzed with high concentrated n-butyl alcohol.

Hyun Kim and Chul Kim⁽⁷⁸⁾ studied the curing reaction of diglycidyl ether of Bisphenol A (DGEBA) with triethylenetetramine (TETA) by the differential scanning calorimetry (DSC). They found that the reaction was affected as the vitrification occurred when the glass transition temperature (T_g) of the reaction mixture exceeded the curing temperature (T_g appeared at temperature 15°C higher than the isothermal curing temperature).

Montserrat⁽⁷⁹⁾ measured the maximum glass transition $T_{g\infty}$ of diglycidyl ether of Bisphenol A (DGEBA) with phthalic anhydride by differential scanning calorimetry in the second scan, he found that this method can eventually produce thermal degradation, decreasing the crosslinking density and the T_g of the sample (T_{g2scan} values are between 98°C and 102°C).

Barralet et. al.⁽⁸⁰⁾ studied the kinetic of the cure reaction for a system containing a diglycidyl ether of bisphenol A (DGEBA) and 1,3-bisaminomethylcyclohexane (1,3-BAC) as a curing agent. By employing differential scanning calorimetry (DSC), used an isothermal approach, he

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have determined the reached conversions at several cure temperatures and the reaction rates. He found that this cure reaction is autocatalytic (T_{cure} from 60 to 110 °C).

Tarifa and Bouazizi⁽⁸¹⁾ measured the glass transition temperature $T_{g\infty}$ of the final networks for epoxy resin diglycidyl ether of Bisphenol A (DGEBA) with diaminodiphenylmethane as crosslinking agent, analysed by Differential Scanning calorimetry (DSC) at various heating rates, they found that the glass transition temperature T_g depends on heating rates (q), ($T_g=189.5$ °C at $q=10$ °C/min and 179.4 °C at $q=1$ °C/min).

Chunet. al⁽⁸²⁾ studied the kinetic of the cure reaction for a system containing diglycidyl ether of bisphenol A (DGEBA) and 4,4-methylene dianiline (MDA) as a curing agent with glutaronitrile (GN) as a reactive additive and hydroquinone (HQ) as an accelerator or a catalyst, by using differential scanning calorimetry (DSC) at various heating rates. He found that the DGEBA/MDA/GN/HQ system followed the second order kinetic. Activation energy was lower than that of the system without HQ. The reaction of nitrile group (GN) with diamine and hydroxyl group resulted in decrease of cross-link and increase of chain length and hydrogen donor (HQ) acted as a catalyst accelerated cure reaction at low temperature and lowered the activation energy.

Roşuet. al⁽⁸³⁾ studied the kinetic of the cure reaction of diglycidyl ether of bisphenol A (DGEBA) and diglycidyl ether of hydroquinone (DGEHQ) epoxy resins in presence of diglycidyl aniline as a reactive diluent and triethylenetetramine (TETA) as the curing agent, by non-isothermal differential scanning calorimetry (DSC) technique at different heating rates. He found that the reactive diluent decreases both the activation energy

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and the cure kinetic parameters (E_a from 69.5 to 59.1 for DGEBA/TETA and 267 to 230 for DGEHQ/TETA).

Sbirrazzuoli et al.⁽⁸⁴⁾ studied the kinetic of the cure reaction of diglycidyl ether of bisphenol A (DGEBA) with meta phenylenediamine (m-PDA) as stoichiometric mixture and as a mixture having an excess of amine, by differential scanning calorimetry (DSC) technique at different heating rates, the model-free isoconversional method was used to estimate the activation energy. He found that in the presence of an excess of the amine the curing is controlled by the primary amine reaction as indicated by practically constant effective activation energy, and in the stoichiometric system shows a decreasing dependence of the effective activation energy (decreases to as low as 20 kJ/mol).

Macanet et al.⁽⁸⁵⁾ studied the kinetic of the cure reaction of epoxy resin based on a diglycidyl ether of Bisphenol A (DGEBA), with poly(oxypropylene) diamine (Jeffamine D230) as a curing agent, was performed by means of differential scanning calorimetry (DSC). Isothermal and dynamic DSC characterizations of stoichiometric (30phr) and sub-stoichiometric (20phr) mixtures were performed. He found that cure kinetics of system DGEBA (30phr), with stoichiometric content of amine, can be successfully described with Kamal model. Catalytic influence of hydroxyl groups formed by epoxy-amine addition on the reaction of cure was determined, and system DGEBA (20phr) with sub-stoichiometric content of amine showed evidence of two separate reactions, second of which was presumed to be etherification reaction. Total heat of reaction for DGEBA (20phr) system was markedly lower than for DGEBA (30phr)

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system, indicating incomplete reaction of epoxy groups (ΔH_T 270 and 430 J g⁻¹ for DGEBA-20a and DGEBA-30a, respectively).

Ghaemy and Sadjady⁽⁸⁶⁾ investigated conducted based on: (1) The study of cure mechanisms and kinetics of diglycidyl ether of bisphenol A (DGEBA) using imidazole (H-MI) and 1-methyl imidazole (1-MI) as the curing agents and, (2) the study of some of the properties of the cured epoxy resins. The cure kinetics of DGEBA was studied using dynamic differential scanning calorimetry (DSC) in various low concentrations (>0.5 mol%) of the curing agents. Kinetic analysis used integral procedure on dynamic DSC data indicates that both H-MI and 1-MI are effective curing agents. They found that the curing reaction of DGEBA with H-MI took place almost 10°C lower than the temperature of its curing reaction with 1-MI, and a small difference between E_a of DGEBA/1-unsubstituted and DGEBA/1-substituted imidazoles systems (3 kJ/mol). Systems, DGEBA/H-MI and DGEBA/1-MI, show similar trends and magnitudes in water absorption (The equilibrium water absorption of both systems was almost 1% by weight), and chemical resistance to acetone and sodium hydroxide solution (4%).

Ghaemy and Shahriari⁽⁸⁷⁾ studied the kinetic and mechanism of cure reaction of diglycidyl ether of bisphenol A (DGEBA) with oxydianiline (ODA) as curing agent in the presence of thermoplastic ABS, used isothermal FTIR and dynamic DSC technique. They found that by FTIR the E_a value of 36 kJ/mol is dropped to 31 kJ/mol in the presence of 30% ABS. Thermodynamic parameters ($\Delta H^\#$, $\Delta S^\#$, and $\Delta G^\#$) for isothermal curing were calculated and the value of $\Delta G^\#$ did not change much with the increasing in the amount of ABS while it increased by increasing isothermal curing temperature, and dynamic curing of the blends in DSC

shows one large exothermic peak, which its position has not changed very much as the amount of ABS is increased to 30%. The E_a values obtained by analyzing DSC data and using different kinetic methods lie in the range of 55-65 kJ/mol, and the values of E_a obtained by analyzing DSC data have shown a small decrease with increasing the amount of ABS.

2.8.2 Review on the Rheological

Matějka⁽⁸⁸⁾ studied curing and gelation of diglycidyl ether of bisphenol A (DGEBA) with poly(oxypropylene) diamine (Jaffamine D 400), by dynamic mechanical measurements. The gel point was determined rheologically and the characteristic value of the loss factor $\tan \delta$ at the gel point. He found that the $(\tan \delta)_{\text{gel}}$, depends on the structure of the polymer, and independent of experimental frequency.

Mijović et al.⁽⁸⁹⁾ studied the time needed to reach at gel point by differential scanning calorimetry (DSC) at different temperatures, for an amine-epoxy system. Flory's method was used to estimate the time, and that time was then compared to the gel time determined from rheological measurements. He found superb agreement.

Laza et al.⁽⁹⁰⁾ focused on studying the effect of the amine concentration on the kinetic, the rheologic characteristics during the crosslinking process, and the dynamic mechanical properties of the system. The curing reaction of the system diglycidyl ether of bisphenol A (DGEBA) with different amine concentrations (TETA) has been studied by means of thermal scanning rheometer (TSR) and dynamic

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mechanical thermal analyser (DMTA). He found that through TSR measurements, the gel time was observed to vary with amine concentration and cure temperature when measurements were carried out under isothermal conditions. The gel time also was found to depend on the heating rate when the measurements were done varying the temperature. The apparent activation energy has a value of 101.48 kJ/mol, this value is greater than those energies calculated from the gel time method.

Núñez et al.⁽⁹¹⁾ measured the gel time for diglycidyl ether of bisphenol A (DGEBA) with metaxylylenediamine (m-XDA) as curing agent, by rheometry and dielectric analysis, gel times obtained by rheometry and dielectric analysis were compared and conversions at gel time calculated. He found a reasonable agreement between the two techniques that lead to gel conversion values very close to those obtained using Flory equation.

Salah et al.⁽⁹²⁾ measured effect of cure temperature on gel time for DGEBA/TETA system with two hardener/resin ratios, by Brookfield viscometer. He found that the gel time decreases with increasing curing temperature for each hardener/resin ratio formulation, and good agreement fitted with the results that were described by Sun model.

CHAPTER THREE EXPERIMENTAL

This chapter describes the equipment, methodologies and experimental procedures, in addition to materials used in this dissertation. The materials used were DGEBA- Epoxy resin and aromatic amine which was meta-phenylenediamine (m-PDA). The DSC technique was used to study the cure kinetics with conditions (80-110°C and 2.5-10°C/min), and Brookfield viscometer was used to measure the viscosity with conditions (80-110°C). The components of the system, the epoxy resin and hardener (curing agent), were carefully weighed on an electronic scale and homogeneously mixed to a ratio of 100:15 phr, shown in Appendix (A).

3.1 Materials

3.1.1 Epoxy Resin

Epoxy resin type epikote 828 which was supplied by Shell Company. Table (3.1) lists the properties of epikote 828 epoxy resin.

3.1.2 Curing agent

Meta-phenylenediamine, also called 1, 3-diaminobenzene, is an aromatic amine, were supplied by Fluka Co. It's a solid state material. It can also be supplied molten in bulk. All forms tend to darken in storage. It is soluble in water, alcohol, and most organic solvents. Typical properties of this agent are shown in Table (3.2)

Experimental

Table (3.1) Epikote828 properties ⁽⁹³⁾

Typical properties	Value
Epoxide equivalent weight ^a	182- 194
Viscosity ^b , at 25 °C, poise	110- 150
Color ^c , Gardner	1 max
Physical form	Clear liquid
Density, g/ml at 25 °C (77 °F)	1.16
Flash point ^d	No flash at 249°C (480 °F)
Vapor pressure,mm Hg at 77 °C (170°F)	0.03
Refractive index at 25 °C (77 °F)	1.573

^aGrams of resin containing one gram equivalent of epoxide. Shell Analytical Method HC-427D-89 (Perchloric Acid Method).

^bShell Analytical Method HC-397A-87 (Determination of the Viscosity of Liquids by Ubbelohde Viscometer).

^cASTM method D-1544-80.

^dASTM D 93.

Table (3.2) m-Phenylenediamine properties⁽⁹⁴⁾

Property	Value
Molecular formula	C ₆ H ₈ N ₂
Molar mass, g/mol	108.1
Melting point, °C	64 - 66
Boiling point, °C	282 - 284
Specific Gravity @ 15°C (59°F)	1.14

Experimental

@ 75°C (167°F)	1.10
Boiling Point (760 mmHg) °C (°F)	283 (541)
Vapor Pressure (mmHg) @ 25°C (77°F) @ 100.0°C (212°F)	0.002 1.0
Flash Point, TOC °C (°F)	138 (280)
Odor	Slight Aromatic
Auto-ignition Temperature °C (°F)	560 (1,040)
Solubility in Water, wt% @ 25°C (77°F) @ 40°C (104°F)	35.1 90.0

3.2 Sample preparation

Epoxy resin and meta-Phenylenediamine were mixed together at room temperature and thoroughly mixed with speed stirrer 60 rpm. The m-Phenylenediamine is solid at room temperature so it must be melted prior to mixing. It was melted in a water bath at temperature (65°C), for approximately 10 minutes. The resin was cured employing stoichiometric ratio. The ratio was prior calculated based on the equivalent weight of the epoxy resin (DGEBA) and meta-Phenylenediamine (m-PDA). Caution was taken to avoid overheating the materials during melting.

In the rheological part, the epoxy resin (DGEBA) and meta-Phenylenediamine (m-PDA) were prepared in stoichiometry ratio. The prepared sample was mixed in a disposable container using a disposable

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stirrer then they were poured into the chamber of the Brookfield viscometer RV+II.

In the kinetic part, the epoxy resin (DGEBA) and meta-Phenylenediamine (m-PDA) were prepared in stoichiometry ratio. Small amounts of the reactive mixture approximately (3-10) mg were poured into aluminum capsules and then subjected to isothermal and dynamic DSC scanning. The reference was an empty aluminum capsule. The purging gas was nitrogen. The flux of nitrogen was set to 100 ml/min.

3.3 Experimental technique

3.3.1 Differential Scanning Calorimetry (DSC)

It is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time,⁽¹⁵⁾. The result of a DSC experiment is a curve of heat flux versus temperature or versus time. There are two different conventions: exothermic reactions in the sample shown with a positive or negative peak, depending on the kind of technology used in the experiment. This curve can be used to calculate enthalpies of transitions). This is done by integrating the peak corresponding to a given transition⁽¹⁶⁾. The experimental method used in this study was Differential Scanning Calorimetry (DSC) Fig (3.1). A Perkin-Elmer DSC-6 instrument with the isothermal or standard data acquisition and analytical software was applied as experimental technique. $T_{g\infty}$ was

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simultaneously measured. The calibration was regularly made using In and Zn standards at each scanning rate being used. All tests



Fig. (3.1) Perkin Elmer Pyris6 Differential Scanning Calorimetry(DSC)

conducted for Differential Scanning Calorimetry in the Department of Material Engineering / University of Technology.

The experiments are categorized in two typical modes:

1. Isothermal scanning.

Experimental

To establish a kinetic model for the cure reaction, a set of isothermal cure curves giving the extent of polymerization as a function of time at a given temperatures has been obtained first.

Cure isotherms were obtained at temperatures of, 80 °C, 90 °C, 100 °C, and 110 °C. Volatile aluminum sample pans were used to reduce losses during heating of the sample in the DSC cell. Actual data collection was initiated and terminated by a computer program which allowed the operator to set the time intervals between data points and accepted input information for data processing. The data acquisition system was then initiated, and the sample was introduced into the DSC cell. The sample pans were inserted into the sample holder at 30 °C, thermal equilibrium at the sample and reference holders were achieved in 1 min, and then heated to the desired curing temperature, T_C , at 40 °C/min. A time record was obtained of both the rate of heat generation, and the integral heat. The latter was obtained by integrating the DSC signal with the help of an analog computer. The reaction was considered complete when the rate curve leveled off to a baseline. The total area under the exotherm curve based on the extrapolated baseline at the end of the reaction gives the isothermal heat of cure. The total reaction enthalpy, ΔH_t , was determined at each T_C by:

$$H_t = \int_0^t \left(\frac{dQ}{dt} \right) dt \quad (3.1)$$

where (dQ / dt) is the instantaneous heat flow during the isothermal scanning.

2. Non- isothermal scanning.

Experimental

In these runs the heating rate were performed at, 2.5, 5, 8, and 10 °C/min, at a temperature interval from (30 °C) to the corresponding T_f , the fully reacted specimens, $T_{g\infty}$, were determined in scanning mode. Scanning experiments on uncured samples were carried out at different heating rates to determine the ultimate heat of cure. The latter was estimated from the area under the scanning exotherm curve with the baseline drawn as a straight line extension of both sides of the scanning exotherm. The total reaction heat is then evaluated by:

$$H_{\text{total}} = \int_0^{t_{fd}} \left(\frac{dQ}{dt} \right) dt \quad (3.2)$$

where t_{fd} is the time required for the completion of the chemical reaction during the dynamic scanning, and $(dQ/dt)_d$ is the instantaneous heat flow during the dynamic scanning.

3.3.2 Rheological characterization

The measured viscoelastic properties can be used to determine the material state throughout the curing process. In order to calculate the viscosity of epoxy resin with Meta-phenylenediamine Brookfield Viscometer Model RV-II+ programmable rotational-type viscometer shown in Fig (3.2) was used.

Brookfield Viscometer has a number of systems designed for several purposes, one of these systems is designed to measure the viscosity during cure and the representation of results in a table in addition to a graph. In this system the viscosity measurement is based on the torque, where the viscosity

Experimental

values are recorded after the arrival of the value of the torque to over ten percent.

10.4 ml of viscous sample were injected into the stainless steel container. SC4-27 type of stainless steel spindle was attached to the viscometer and spindle depth into the epoxy was adjusted to the notch on the spindle shank, and the chamber used is disposable HT-2DB, both of them are specially designed for measuring sticky fluids.. The clearance between the spindle periphery and the chamber inner wall is 3.15 mm. The viscosity readings at constant temperatures of 80 °C, 90 °C, 100 °C and 110 °C with different velocities of 100, 10, 1, 0.1 and 0.01 rpm were recorded for each set of sample. This change in velocities is to protect the device from breakage. The viscometer is a fully computer controlled device with a well-defined menu system. The output data are viewed on a monitor in graphical and table form during the measuring time. For isothermal measurements, the sample chamber was preheated to the desired temperature and stabilized at that temperature for five minutes. Two systems were used to control the temperature, water system and oil system. Viscosity measurement begins after placing the sample in the chamber for measuring, then reads the viscosity with time for the epoxy system at different temperatures.

Experimental



Fig.(3.2) RV+II Programmable Brookfield Viscometer

Experimental

CHAPTER FIVE

CONCLUSIONS AND FUTURE WORK

5.1. Conclusions

1. The isothermal cure reaction heat increases with the increment of cure temperature.
2. The maximum degree of cure at isothermal cure temperature 110 °C is 0.9.
3. In the earlier stage of the isothermal cure reaction, the cure rate at the higher temperatures is faster than the cure rate at the lower temperatures.
4. Kamal with diffusion model can provide a good predication of experimental data.
5. The kinetic rate constants K_1, K_2 , and m increase with the increment of cure temperature while the orders of reaction n and $(m+n)$ decrease.
6. The final $T_{g\infty}$ increase with the increment of degree of cure.
7. The dynamic cure reaction heats decrease with increment heating rate while the T_p increase.
8. In the modeling method based on the Kissinger and Ozawa, the obtained activation energy and pre-exponential factor, slightly difference between them.

CONCLUSIONS AND FUTURE WORK

9. The isoconversional method provides activation energy along for process, and E_a decreases with increment conversion.
10. As isothermal temperature increases, the gel time of cure process decreases.
11. Sun model agrees very well with the experimental data.
12. The critical time in the model decreases with the increment of the isothermal temperature.
13. The activation energies determined by the gel time, and critical time are close each other.
14. The gel time obtained by DSC different those obtained by rheological measurement.

5.2 Suggestions for Future Work

1. Using the same epoxy resin systems to study mechanical properties with and without enhancement materials.
2. Studying the thermal stability of the same system by TG.
3. Using other instruments such as FTIR (Fourier Transform Infrared Spectrometry), to study the cure reaction, and comparison with DSC.
4. Measuring uncured glass transition temperature.

CONCLUSIONS AND FUTURE WORK

5. Minimum viscosity measurements could be improved through the use of a technique sensitive to low viscosity like shear rheometry.

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Appendix A

Calculation of Stoichiometric Ratios

According equations (2.1) and (2.2)

$$\text{Amine } H \text{ eq wt} = \frac{108.14}{4} = 27 \text{ g/eq}$$

$$\text{phr of amine} = \frac{27 * 100}{186} = 14.5 \cong 15 \text{ g}$$

AppendixB

Table B.1 Exothermic peak maxima, T_p , and total heat of reaction, ΔH_{tot} of DGEBA curing with aromatic amine

β ($^{\circ}\text{C min}^{-1}$)	T_p (K)	ΔH_{tot} (J/g)	Average ΔH_{tot} (J/g)
2.5	417	576	563.5
5	430	565	
8	440	559	
10	448	554	

Table B.2 Activation energy E_a of epoxy DGEBA with phenylenediamine from multiple scanning rate methods.

model	exponential factor	E_a (kJ mol^{-1})
Ozawa	21.36	70.7
kissinger	7.22	63.6

AppendixB

Table B.3 Data of $\ln(\beta)$ and T for DGEBA/m-phenylenediamine at different conversions.

β ($^{\circ}\text{C min}^{-1}$)	Conversion T (k)			
	0.2	0.4	0.6	0.8
10	425	436	446	459
8	416	427	435	447
5	407	417	426	437
2.5	397.5	406	414	425

Table B.4 activation energy of curing epoxy DGEBA with m-phenylenediamine at different conversion

Conversion	Ea (kJ/mol)
0.2	68
0.4	65.5
0.6	64.7
0.8	63.9

AppendixC

Table C.5 Total heat of reaction, ΔH_t of DGEBA curing with m-phenylenediamine from isothermal

T (°C)	ΔH (J/g)	ΔH average
110	507	475
100	493	
90	462	
80	439.5	

Table C.6. Time at maximum rate of reaction t_p and maximum rate of reaction r_p at different curing temperatures.

T (°C)	t_p (min)	r_p (s ⁻¹)
110	9.9	0.00075
100	17.5	0.00047
90	32	0.00029
80	48.9	0.00018

AppendixC

Table C.7. Kinetic parameters as determined from the autocatalytic kinetic model for epoxy (DGEBA) with m-phenylenediamineat various curing temperatures.

T (°C)	k_1 ($\times 10^5$ s^{-1})	k_2 ($\times 10^4$ s^{-1})	m	n	m+n	c
110	40.09	10.48	0.95	0.78	1.73	50.61
100	24.18	7.69	0.94	0.87	1.81	45.75
90	11.2	6.05	0.85	0.97	1.82	57.99
80	5.6	4.94	0.85	1.2	2.05	61.44
E_{a1} (kJ/mol)		$A_1(s^{-1})$	E_{a2} (kJ/mol)		$A_2(s^{-1})$	
75.31		15.877	28.12		1.9347	

Appendix D

Table D.8. Gel Time at Different Temperatures and the Activation Energy

Temperature (°C)	80	90	100	110
t_{gel} (sec)	2760	1200	810	300
E_a (KJ/mol)	79.07			
Pre-exponential factor (s^{-1})	9.19			

Table D.9. kinetic Parameters in viscosity model (2.28)

T (°C)	t_c (s)	k (s^{-1})
80	3600	0.23
90	1380	0.65
100	900	2
110	360	4.4
E_a (KJ/mol)	79.46	
Pre-exponential factor (s^{-1})	5.66	

AppendixE

Table E.10 Gelation and different cure temperatures obtained by rheological and thermal measurements

T (°C)	Gelation time(min) (rheology)	Gelation time(min) (DCS)
80	46	53
90	20	31
100	13.5	20
110	5	11

الخلاصة

تم دراسة حركيات الإنضاج (cure kinetic) ودرجة حرارة التحول الزجاجي (Tg) والريولوجي (Rheology) لنظام راتنج الأيبوكسي المحضر من تفاعل (DGEBA) مع الأمينات العطرية (m-PDA) عن طريق جهاز المسح التفاضلي (Perkin Elmer Pyris 6) وجهاز قياس اللزوجة (Brookfield viscometer RV-II) بالاعتماد على نسبة الخلط الوزنية (15:100).

فحوصات حركية الانضاج ودرجة حرارة الانتقال الزجاجي تمت بجهاز المسح التفاضلي وبثبوت درجة الحرارة (isothermal), درجات الفحوصات التي اعتمدت هي (80,90,100,110) °م, كذلك تم محاكاة حركية الإنضاج باستخدام موديل كمال المعدل مع عامل الانتشار (diffusion factor), حيث اظهرت النتائج بان نسبة التحول تزداد بزيادة درجة الحرارة واعلى تحول تم الحصول عليه هو (0.9) عند درجة الحرارة (110) °م, وقد لوحظ أيضا هناك تطابق جيد بين نتائج الفحوصات مع تلك التي تم الحصول عليها من الموديل المفروض. كما ان درجة حرارة التحول الزجاجي (Tg) تزداد بزيادة درجة التحول.

كما انفحصت حركية الانضاج تمت بجهاز المسح التفاضلي بطريقة تغير درجات الحرارة (non isothermal), حيث تم حساب طاقة التنشيط بطريقتي (Kissinger) و(Ozawa), حيث اعطت طريقة (Ozawa) قيمة اعلى بقليل من طريقة (Kissinger). كما طبقت طريقة (isoconversional) حيث اعطت مدى من طاقات التنشيط مع التحول, حيث اظهرت تناقص بالطاقة مع زيادة درجة التحول.

الخصائص الريولوجية لنظام راتنج الأيبوكسي درست بواسطة جهاز قياس اللزوجة (Brookfield viscometer) ولأربع درجات حرارية هي (80,90,100,110) °م. لوحظ عند تطور تفاعل النضوج النظام يصبح في حالة هلام, وقت تشكل المادة الهلامية حسب عند كل درجة حرارة, النتائج اظهرت وقت الهلام يتناقص مع زيادة درجة الحرارة. طاقة التنشيط تم حسابها في وقت الهلام بواسطة معادلة ارينيوس. منحنيات اللزوجة تم محاكاتها بواسطة موديل (Sun mode), وقد اظهرت النتائج بوجود تطابق ممتاز بين النتائج العملية والموديل المقترح. كما لوحظ ايضا ان وقت تشكل الهلام المحسوب

من حسابات جهاز المسح التفاضلي بالاعتماد على معادلة فلوري يختلف عن الوقت المحسوب من
نتائج الريولوجي



وزارة التعليم العالي والبحث العلمي

الجامعة التكنولوجية

قسم الهندسة الكيميائية

دراسة الخواص الريولوجية والحركية لأنضاج راتنجات الايبوكسي مع ثنائي الأمين الفينيلين

رسالة مقدمة الى

قسم الهندسة الكيميائية في الجامعة التكنولوجية كجزء من متطلبات

نيل درجة ماجستير علوم في الهندسة الكيميائية / وحدات صناعية

إعداد

بشار جواد كاظم

(بكالوريوس هندسة كيميائية 2004)

بإشراف

أ. م. د نجاه جمعة صالح

ايلول 2011 م

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