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Abstract

Thermoplastic toughening of epoxy resins had aroused considerable interest in the past few decades. Functionalized as well as nonfunctionalized thermoplastics have been extensively used to toughen epoxy resins. The ultimate properties of the blends are strongly dependent on the cure conditions employed. Investigation of the cure kinetics is therefore very important in predicting the ultimate properties. Kinetic analysis gives information regarding the extent of cure, curing mechanism, activation energy, etc. Techniques such as differential scanning calorimetry, Fourier transform infrared spectroscopy, dielectric relaxation spectroscopy, etc. are useful tools for kinetic analysis. Various models have been developed for the evaluation of cure kinetics. This chapter summarizes the various aspects of the kinetics of epoxy resin/thermoplastic blends.

Keywords

Cycloaliphatic amine-cured resins • Differential scanning calorimetry • Epoxy resin/thermoplastic blends • Dynamic kinetic analysis • Isothermal kinetic analysis • Epoxy resins • Curing • Etherification • Flynn–Wall–Ozawa method • Hardeners • Isothermal kinetic model • Kamal model • Kinetic analysis • Kinetic modeling • Kissinger method • Polyoxypropylene diamine (POPDA) • Reaction-induced phase separation • Transamidation reaction • Vitrified state

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Contents

Introduction	650
Curing of Epoxy Resins	650
Kinetic Modeling	655
Kamal Model (Isothermal Kinetic Model)	655
Kissinger Method (Dynamic Kinetic Model)	656
Flynn–Wall–Ozawa Method (Dynamic Kinetic Model)	657
Kinetic Analysis	657
Kinetic Analysis Using DSC	658
Epoxy Resin/Thermoplastic Blends	659
Dynamic Kinetic Analysis	660
Isothermal Kinetic Analysis	662
Conclusions	669
References	670

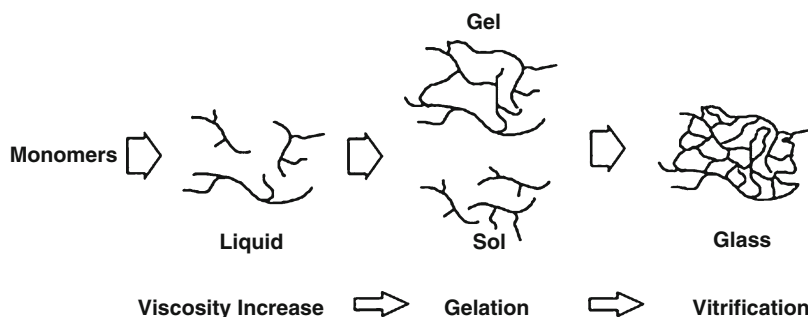
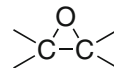
Introduction

Epoxy resins were made available commercially in 1946. Since then, their technology has grown to such an extent that they were accepted as workhorse raw material among the various thermosetting resins. Epoxy resin technology is extensively used in a variety of applications ranging from coatings to military and aerospace applications due to their extraordinary mechanical properties and good handling characteristics (May 1988). Adhesion to a variety of substrates, low cure shrinkage, processing flexibility, etc. are a few important properties of epoxy resins to mention (Skiest 1978; Pascault and Williams 2010). Epoxy resins are now available in various physical forms. The diglycidyl ether of bisphenol A (DGEBA) is the widely used resin among the different types of epoxy resins commercialized. Epoxy phenol novolac (EPN) and epoxy cresol novolac (ECN) resins are also commercially important aromatic glycidyl ether resins. The physical state of the resins changed as the functionality changed. Multifunctional epoxy resins are either highly viscous or low melting solids. Such resins are mainly used in high-performance materials. Multifunctional glycidyl amino resins like triglycidyl-p-aminophenol (TGAP) and tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) are used for such applications.

Curing of Epoxy Resins

Epoxy resins are characterized by a three-membered ring known as epoxy, epoxide, oxirane, or ethoxylene group, consisting of an oxygen atom attached to two interconnected carbon atoms as shown in Fig. 1.

The strained three-membered ring structure makes epoxy resin reactive. Hence it is attacked by nucleophilic and electrophilic reagents. The ultimate properties of epoxy resin are achieved by converting them to insoluble and infusible network. This is achieved by reaction with various chemical compounds known as curing

Fig. 1 Epoxy group**Fig. 2** Schematic representation of the physical changes occurring during the curing of epoxy resin

agents or hardeners. A large number of compounds with active hydrogen atoms are capable of reacting with epoxy resin. Amines, phenols, alcohols, thiols, carboxylic acids, acid anhydrides, etc. are potential coreactive cross-linking agents for epoxy resin. However the choice depends on the availability, processability, handling characteristics, and final properties of the cured resin. For industrial application, the final performance and processing aids determine the selection of curing agent (Young and Chuang 1995; Holmberg and Berglung 1997; Abraham and Mc Ilhagger 1998; Pascault et al. 2002).

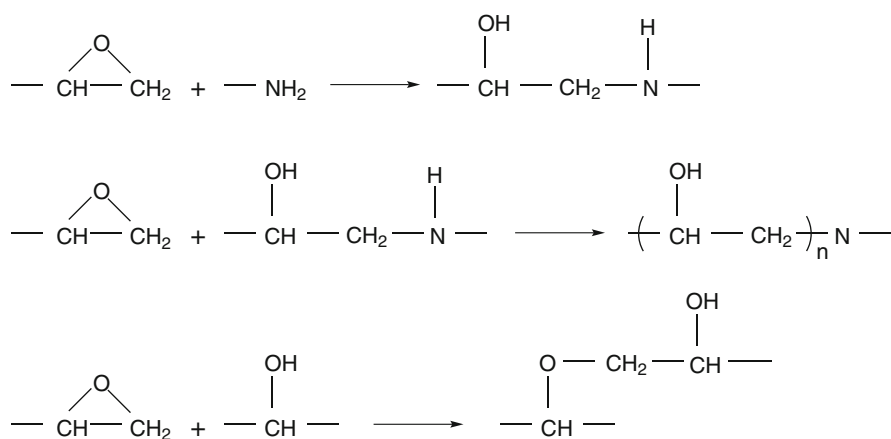
The ultimate properties can be tailored as per user requirement by judicious selection of the resin and curing agent. The functionality of the reactants controls the network formation and cross-link density. The network structure, curing degree, curing time, and cure temperatures determine the physical properties of the cured epoxy resins (Montserrat and Málek 1993; Caçcaval et al. 1997; Jagadeesh et al. 2000; Roşu et al. 2001). The epoxy resin and curing agent forms linear chains in the early stages of curing. As the reaction proceeds further, branches will form and finally it emerges as a highly cross-linked structure. During curing, the molecular weight of epoxy resin increases rapidly and becomes linked together into networks of infinite molecular weight.

Many physical changes occur during curing of epoxy resins. Usually the processing of epoxy resin is done in the liquid state. If the resin is in the solid state, it is melted and processed. The low viscosity liquid first forms a sol. As cross-linking reaction proceeds, it becomes a gel, and further cross-linking leads to a highly cross-linked structure called glassy state or vitrified state. The curing reaction is accompanied by a gradual increase in the viscosity of the epoxy resin-curing agent mixture. Once the system gels, the curing reaction becomes slow due to the increase in viscosity. A schematic representation of the physical changes during curing reaction of epoxy resin is given in Fig. 2. The handling, processing, and development of ultimate properties are dependent on gelation and vitrification.

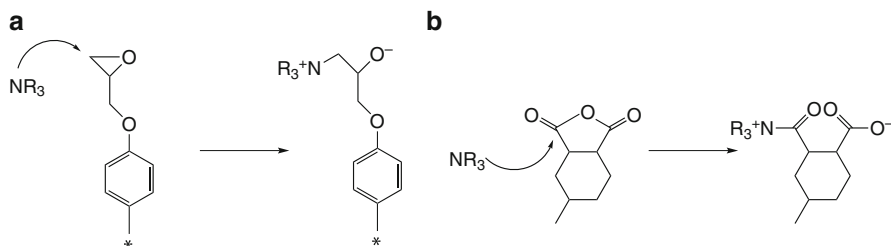
Although a large number of compounds are reactive toward epoxy group, amines and anhydrides are the most commonly used curing agents. A range of aromatic and aliphatic amines were used for curing epoxy resins. The ultimate properties of the resin depend on the nature of the amine used. Aliphatic amine offers ambient cure temperature and low viscosity. The cured resins have good physical properties and excellent chemical and solvent resistance. They retain their properties up to 100 °C for extended periods. These properties are controlled by the mixing ratio. However the toughness of the cured resin is low. Cycloaliphatic amine-cured resins have better toughness than aliphatic amine-cured resins. The reactivity of cycloaliphatic amine toward epoxy is less compared to acyclic aliphatic amines. Hence these systems have longer pot life. Aromatic amines are less reactive than aliphatic and cycloaliphatic amines due to the delocalization of electrons. Hence these systems have long pot lives and need elevated temperature for curing. But they have better chemical and thermal resistance than aliphatic and cycloaliphatic amine-cured resins. Also they retain their properties at temperatures as high as 150 °C for longer times. Another important class of curing agents is acid anhydride. They usually require catalyst and post curing for optimum performance. Other characteristics of anhydride curing are low viscosity, low exothermic heat of reaction, and long pot life. They extend excellent mechanical and electrical properties too.

The reaction of epoxide with amine involves several reactions like addition of amine to epoxide, homopolymerization of epoxy by etherification or ionic polymerization, cyclisation, and various side transformations and degradation reactions. In most cases, the addition of amine is the predominating reaction. The reaction between epoxy resin and an amine-curing agent is given in Scheme 1.

Reaction of primary amine with epoxy yields a secondary amine and secondary hydroxyl group. The secondary amine in turn reacts with an epoxy to give a tertiary amine and two secondary hydroxyl groups. The last step is the etherification;



Scheme 1 Reaction between amine-curing agent and epoxy resin



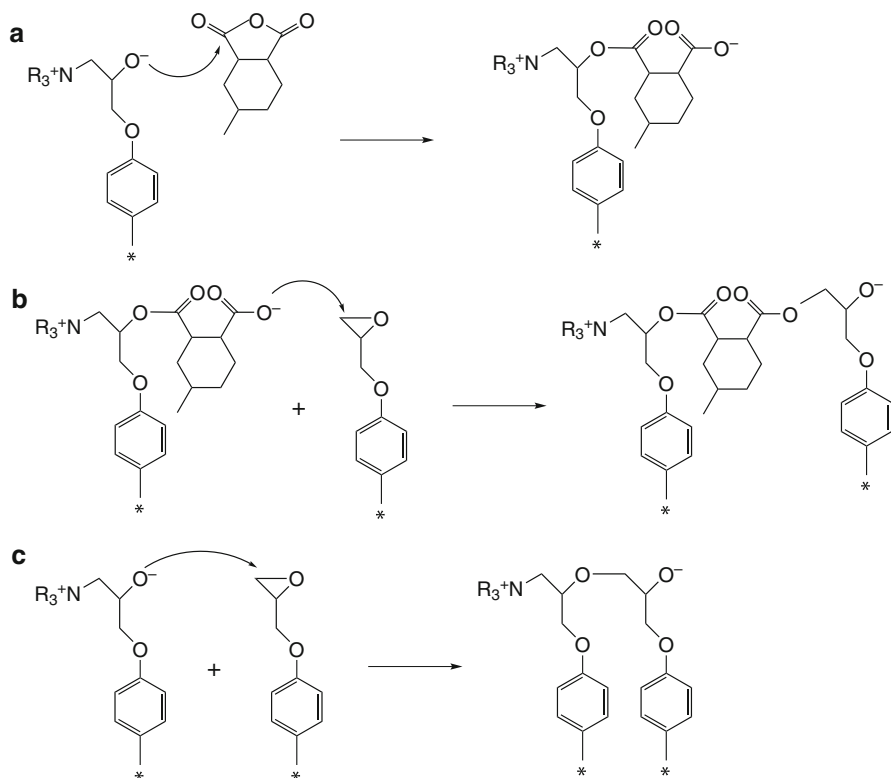
Scheme 2 Initiation step of the curing of epoxy-anhydride formulations with tertiary amines by nucleophilic attack (a) to an oxirane ring and (b) to a cyclic anhydride

however, the tendency of the etherification reaction depends on the curing temperature, basicity of the diamine, and the initial epoxy/amine ratio (Lunak and Dusek 1975; Riccardi and Williams 1986).

The reactivity of amine toward epoxy curing changed with the structure and other groups on the amine. Experiments using size exclusion chromatography and viscosity measurements on the reactivity of amine toward DGEBA epoxy resin revealed that DDM was the most reactive. The reactivity decreased in the order DDM > BAPP > BAPS > 3,3'-DDS > 4,4'-DDS, where DDM, BAPP, BAPS, 3,3'-DDS, and 4,4'-DDS represent 4,4'-diaminodiphenylmethane, 2,2'-bis[4-(4-aminophenoxy)phenyl]propane, bis[4-(4-aminophenoxy)phenyl]sulfone, 3,3'-diaminodiphenylsulfone, and 4,4'-diaminodiphenylsulfone, respectively. Basicity of the amines was the controlling factor. In DDS, sulfone group, being an electron withdrawing group, decreased the basicity of the diamine. 4,4'-DDS is least reactive because the electron transfer from -NH_2 to -SO_2 is the easiest for *para* substitution. BAPP and BAPS are more reactive than DDS and less reactive than DDM due to the action of phenoxy group (Grillet et al. 1989). The reactivity of amine decreased in the order DDM > MDEA > DDS > MCDEA for DGEBA epoxy resin (Reydet et al. 1995). MDA, MDEA, and MCDEA exhibited same secondary to primary amine reactivity ratio of 0.65, but DDS exhibited a different value (0.45). The lower value is due to the lower number of stable conformations afforded by -SO_2 group in comparison to -CH_2 group. MDEA and MCDEA represent 4,4'-methylenebis(2,6-diethylaniline) and 4,4'-methylenebis(3-chloro-2,6-diethylaniline), respectively.

The anhydride curing of epoxy resin is rather complex due to the large number of competitive reactions involved in the curing reaction. The reactions become more complicated in the presence of accelerators, which is often necessary when anhydrides are used as the curing agent. Many reaction schemes have been proposed in the presence and absence of accelerators (Dusek et al. 1982; Khanna and Chanda 1993, 1996; Teil et al. 2004; Fernandez-Francos et al. 2014). Two possible initiation steps are there as shown in Scheme 2. The tertiary amine can nucleophilically attack the epoxy ring or the anhydride.

It is believed that Scheme 2a, the reaction of alkoxide ion with anhydride to form carboxylate anion, takes place. The anion then reacts with epoxy group to give another alkoxide ion (Scheme 3a, b). In the presence of excess epoxy groups, the



Scheme 3 Propagation of the reaction by (a) nucleophilic attack of the alkoxide anion to an anhydride, (b) followed by nucleophilic attack of the carboxylate anion to an epoxy group, or (c) nucleophilic attack of the alkoxide anion to an epoxy group

alkoxide anion can add to another epoxy group (Scheme 3c). Presence of excess epoxy is necessary because the formation of resonance-stabilized carboxylate anion is highly favorable.

In an alternative scheme, the epoxy group reacts directly with the epoxy group in the propagation step. Finally the initiator is regenerated by unimolecular elimination of the carboxyl-amine ion pair followed by a proton transfer (Mauri et al. 1997).

The hydroxyl group can react with anhydrides either in the presence or absence of a catalyst-like tertiary amine giving rise to a carboxylic ester. The carboxylic acids can then react with epoxy groups to give rise to β -hydroxy esters in the presence of catalysts (Trappe et al. 1991; Blank et al. 2002; Rocks et al. 2004; Foix et al. 2009). When tertiary amines are used as catalysts, the mechanism involved the formation of a carboxylate anion (Blank et al. 2002). In addition to the above mechanisms, other reactions like transesterification can occur in the presence of carboxylic acids (Matějka et al. 1985). From the above schemes, it is clear that the anhydride curing of epoxy resin is quite complicated.

Kinetic Modeling

Two types of equations are used for kinetic modeling; one is based on the reaction pathway and the other is the phenomenological kinetic equations (Pascault et al. 2002). The model proposed by Horie et al. (1970) and simplified by Kamal and Sourour is the most widely used phenomenological kinetic equation (Kamal and Sourour 1973; Sourour and Kamal 1976). The Kissinger and Flynn–Wall–Ozawa models are also used in the kinetic analysis of epoxy curing.

Kamal Model (Isothermal Kinetic Model)

This model is simple to use and does not need prior knowledge of the reaction mechanism. It has been used widely in various thermosetting systems for resin transfer molding (RTM), filament winding, resin injection molding (RIM), micro-wave curing, etc. (Karkanias et al. 1996; Halley and Mackay 1996; Bonnaud et al. 2000; Um et al. 2002; Naffakh et al. 2005). The model assumes that the epoxy–amine reaction is catalyzed by the hydroxyl groups formed during curing and those existing in the resin or by acidic impurities present in the system. Also the degree of reactivity of primary and secondary amine hydrogens toward epoxy group is the same. The kinetic equation is

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (1)$$

where k_1 is the rate constant for the reaction catalyzed by groups initially present in the resin, k_2 is the rate constant for the reaction catalyzed by hydroxyl groups formed during the reaction, and $m + n$ gives the overall order of the reaction.

In a modified version of the Kamal equation, it was assumed that the curing reaction followed second-order process. But as cure reaction proceeds, the glass transition temperature T_g of the system approaches the curing temperature T_{cure} . In addition, the viscosity of the system will also increase. When T_g approaches T_{cure} , the reaction becomes diffusion controlled, and the reaction rate becomes zero before complete reaction. So the final conversion is dependent on the cure temperature. The effect of cure temperature is incorporated in the models replacing the term $1 - \alpha$ with $\alpha_{\text{max}} - \alpha$, where α_{max} represents the final conversion reached at the investigated temperature (Musto et al. 1999).

The equation becomes

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(\alpha_{\text{max}} - \alpha)^n \quad (2)$$

Plot of $\frac{d\alpha}{dt} / (\alpha_{\text{max}} - \alpha)$ versus α gives a straight line with intercept k_1 and slope k_2 . These constants follow the Arrhenius relationship with cure temperature.

$$k_i = A_i e^{-E_i/RT} \quad (3)$$

$$i = 1, 2$$

In these models, the kinetic parameters were determined using least squares method without any constraints. Toward the end of the curing reaction, the reaction becomes diffusion controlled. In order to incorporate diffusion control, a semi-empirical equation was used. When degree of cure reaches critical value α_c , diffusion becomes the dominant phenomenon, and rate constant k_d is given by

$$k_d = k_c e^{-C(\alpha - \alpha_c)} \quad (4)$$

where k_c is the rate constant for chemical kinetics and C is the diffusion coefficient.

According to this equation, diffusion control begins when α becomes equal to α_c . But in actual conditions, the onset of diffusion control is a gradual process, and there is a certain curing stage where both chemical and diffusion factors are controlling the reaction.

The overall effective rate constant k_e is given by

$$\frac{1}{k_e} = \frac{1}{k_d} + \frac{1}{k_c} \quad (5)$$

The diffusion factor $f(\alpha)$ is given by

$$f(\alpha) = \frac{k_e}{k_c} = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \quad (6)$$

The diffusion factor is the ratio of the experimental reaction rate to the reaction rate predicted by Kamal model. When α is much smaller than critical value ($\alpha \ll \alpha_c$), $f(\alpha)$ approximates unity, and the reaction is kinetically controlled, and diffusion effect is negligible. As α approaches α_c , $f(\alpha)$ begins to decrease and approaches zero as the reaction effectively stops. The effective reaction rate at any conversion is equal to the chemical reaction rate multiplied by $f(\alpha)$. The values of α_c and C are determined by the nonlinear regression analysis to $f(\alpha)$ versus α plot.

Kissinger Method (Dynamic Kinetic Model)

In the Kissinger method, the activation energy is obtained from the maximum reaction rate where $\frac{d}{dt}(d\alpha/dt)$ is zero under a constant heating rate condition.

$$\frac{d \left[\ln \left(q/T_p^2 \right) \right]}{d(1/T_p)} = -\frac{E}{R} \quad (7)$$

where T_p is the maximum rate temperature, q is the constant heating rate, E is the activation energy, and R is the gas constant. A plot of $\ln(q/T_p^2)$ versus $1/T_p$ gives the activation energy without a specific assumption on the conversion-dependent function.

Flynn–Wall–Ozawa Method (Dynamic Kinetic Model)

In this method, it is assumed that the extent reaction is proportional to the heat generated during the reaction. The reaction rate is expressed as

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (8)$$

where t is the time, $k(T)$ is the Arrhenius rate constant, and $f(\alpha)$ is a function that depends on the reaction mechanism. The integrated form of the above equation is

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = k(T)t \quad (9)$$

where $g(\alpha)$ is the integrated form of the conversion dependent function.

Flynn–Wall–Ozawa modified the equation for $g(\alpha)$ as

$$\log(q) = \log \left[\frac{AE}{g(\alpha)R} \right] - 2.315 - \frac{0.457E}{RT} \quad (10)$$

where A is a pre-exponential factor, q is the heating rate, R is the universal gas constant, and T is the temperature.

The activation energy (E) at different conversion can be calculated using this equation. The activation energy can be calculated from the slope $\frac{0.457E}{RT}$, obtained from a plot of $\log(q)$ versus $1/T$. It is also assumed that the degree of conversion is independent of heating rate once exothermic peak is reached (Salla and Ramis 1996).

Kinetic Analysis

Analytical techniques such as differential scanning calorimetry (DSC) (Montserrat and Martin 2002; Ivankovic et al. 2003; Swier et al. 2004), thermal scanning rheometry (Laza et al. 1999), dielectric spectroscopy (Levita et al. 1996), Raman spectroscopy (Overbeke et al. 2001), and Fourier transform infrared spectroscopy (FTIR) (George et al. 1991; Varley et al. 1995; Mijović et al. 1996) have been used to monitor the curing reaction of epoxy resins. Extensive kinetic analysis of the curing reaction revealed that the epoxy-amine curing reaction followed an autocatalytic mechanism (Vyazovkin and

Sbirrazzuoli 1996; Shen et al. 2001; Zvetkov 2001). The curing kinetics was influenced by the changes in the chemical structure of curing agents (Kim and Lee 2002).

Kinetic Analysis Using DSC

DSC is a convenient and simple-to-use tool for monitoring cure reaction since precise results were obtained with a small amount of sample in a relatively short time span. The basic assumption is that the heat evolution recorded by DSC is proportional to the extent of consumption of the functional groups, such as the epoxide groups in the epoxy resin or amine groups in the curing agent. DSC has two advantages: (i) it is the reaction rate method that permits to measure with great accuracy both the rate of reaction and degree of conversion, and (ii) the DSC cell may be considered as a mini-reactor without temperature gradient. Both isothermal and dynamic measurements can be used to follow the cure reaction. The dynamic measurements are fast compared to isothermal measurements. DSC kinetics provides heat flow and heat generation data required for the solution of the heat/mass transfer equation. The basic assumption for the application of DSC technique to the cure of the epoxy resin is that the rate of reaction is proportional to the measured heat flow (ϕ).

$$\text{Rate of reaction, } \frac{d\alpha}{dt} = \frac{\phi}{\Delta H} \quad (11)$$

where ΔH is the enthalpy of curing reaction.

The curing involves several reactions including primary and secondary amine attack on epoxy group, homopolymerization, etherification, and degradation (Schiraldi and Baldini 1983). This makes the analysis of polymerization kinetics from dynamic DSC measurements difficult. But in isothermal mode, the overall process can be analyzed, and more information regarding the kinetics can be obtained (Sourour and Kamal 1976). The isothermal measurements provide more reliable heat of reaction and kinetic parameters (Salla and Ramis 1996; Gonis et al. 1999).

The important parameters required for kinetic analysis are the total heat of the reaction ΔH_{tot} and the fractional conversion α at time t . The ΔH_{tot} can be obtained from dynamic and isothermal methods in the following ways. (i) ΔH_{tot} was taken as the average of the enthalpy values obtained from the calorimetric measurements at different heating rates in dynamic mode. (ii) The sample is analyzed isothermally at a particular temperature, and after the measurement, the same sample was analyzed in dynamic mode for examining the completeness of the curing reaction. The sum of the heat of reaction obtained from isothermal measurement and the subsequent dynamic mode is taken as ΔH_{tot} .

In order to calculate the conversion (α) at time t , the heat of reaction at time t (ΔH_t) is required. The isothermal scan of the sample was done and the curve was integrated at different times. From the area of the curve at a particular time, the heat of reaction at that time interval can be calculated. In another approach, the sample

was cured isothermally and the curing reaction was quenched at different time intervals. The dynamic DSC scan of the quenched samples gave the residual heat of reaction. The difference between the total heat of reaction and the residual heat will give the value of ΔH_{tot} . From these values, the conversion α at time t is calculated using the equation

$$\alpha = \frac{\Delta H_t}{\Delta H_{tot}} \quad (12)$$

Epoxy Resin/Thermoplastic Blends

Blending two or more polymers is an easy and cost-effective way of developing materials with desirable properties. The ultimate properties of the blends can be manipulated according to end use by the proper selection of component polymers. As mentioned in the introduction, the properties of epoxy resin are attributed to their high cross-link density. Because of high cross-link density, these materials have very low resistance to crack initiation and propagation. Therefore it is very important to increase the toughness of these materials without causing major losses in other desirable properties. Of all the methods that have been considered and adopted in an attempt to alleviate the brittle characteristics of epoxy resin, elastomeric and thermoplastic (TP) modifications were found to be most successful. The frequently used thermoplastics are polysulfone (Andrés et al. 1998; Mimura et al. 2000), polyether imide (PEI) (Reydet et al. 1997; Bonnet et al. 2001), polyether ether ketone (Pasquale et al. 1997; Francis et al. 2005, 2006a, b, 2007), polycarbonate (PC) (Liello et al. 1994), polyethylene terephthalate (Ochi et al. 1989, 1994), etc.

The addition of a thermoplastic modifier generates further complexities in the already complicated system. The following events could happen upon adding a thermoplastic to the epoxy resin:

- Increase in the viscosity of the system
- Interaction of the functional groups on thermoplastic with epoxy resin
- Reaction-induced phase separation (RIPS) upon curing
- Entrapment of some thermoplastic in epoxy phase and vice versa

Other factors such as gelation, vitrification, and change from chemical kinetic to diffusion control with the advancement of curing also influence the processing and ultimate properties of the blend.

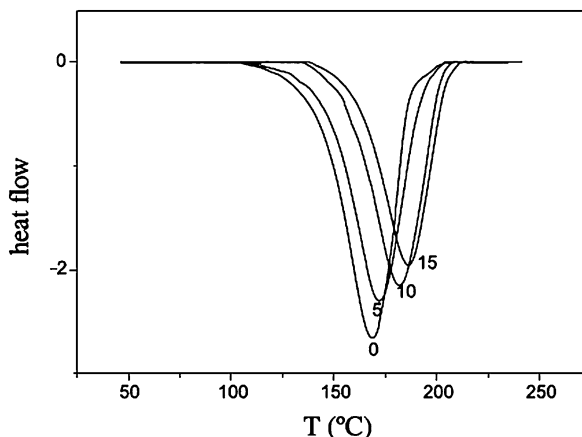
The cured epoxy resin/thermoplastic blends as well as the epoxy resin result from the irreversible reaction of the reactive species in the formulation. This means that the properties once fixed cannot be altered at a later stage. Thus there is an intimate relationship between the ultimate properties, structure, and reaction kinetics. Kinetic parameters provide significant information about the final structure of the network, properties, and material processability. Hence the kinetic studies of epoxy resin/thermoplastic blends are extremely important.

Dynamic Kinetic Analysis

Extensive research has been done on the kinetics of thermoplastic-toughened epoxy resin. The presence of thermoplastic did not alter the autocatalytic mechanism observed in epoxy resin curing (Barral et al. 2000a; Francis et al. 2003, 2006c; Naffakh et al. 2005; Cabezudo et al. 2006; Prolongo et al. 2007; Lopez et al. 2009; Jyotishkumar et al. 2010, 2012; Jyotishkumar and Thomas 2011; Xu et al. 2012). But the extent of cure, maximum rate of the reaction, conversion at maximum rate, activation energy, etc., are affected by the curing conditions and the amount of thermoplastic present in the blends. The kinetic parameters are also influenced by the thermoplastic used to toughen epoxy resin. Figure 3 represents the heat flow versus temperature curves for a thermoplastic-toughened epoxy resin. The exothermic peak temperature (T_p) shifted to higher values in the blends. The increased shift in T_p is due to the decrease in the polymerization rate due to a dilution effect where the presence of thermoplastic reduces the concentration of reactive groups, thus decreasing the cure rate (Rusli et al. 2014). The decrease in reaction rate can also be due to the decrease in the amount of catalytic group. For example, in nadic methyl anhydride (NMA)-cured tetrafunctional epoxy resin, benzyl dimethylaniline (BDMA) was used as the catalyst. But the carboxyl end group in perfluoroether oligomer used as modifier reacted with the catalyst to form quaternary ammonium salt decreasing the amount of catalyst which in turn reduced the final conversion (Musto et al. 2001).

Shoulder peaks are not generally expected in the thermograms. Cyanate ester-cured DGEBA epoxy resin modified with phenolphthalein poly(ether ketone) (PEK-C) presents a different behavior. It is observed from the dynamic scan of the blends in Fig. 4 that the initial temperature (T_i) and T_p decreased with increase in PEK-C content. A shoulder peak was also observed in the dynamic scan. These changes from the expected behavior are due to the fast curing rate of the epoxy resin

Fig. 3 Dynamic thermograms for neat and epoxy matrices with several contents of polyethersulfone (Reprinted from Eur Polym J (2001) 37:1863 with permission from Elsevier)



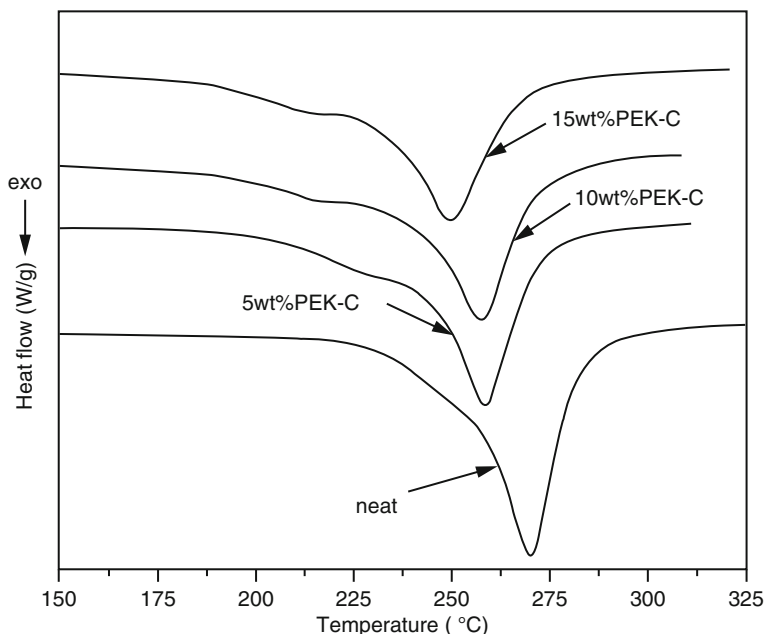


Fig. 4 Dynamic DSC thermograms of epoxy/PEK-C blends at a heating rate of 10 °C/min (Reprinted from *J App Polym Sci* (2009) 111:2590 with permission from Wiley)

as a result of the accelerated trimerization reaction of cyanate monomers by the phenolic end groups on PEK-C (Li et al. 2009).

Two distinct peaks are explicit in the dynamic DSC thermograms (Fig. 5) of a bisphenol A polycarbonate-modified DGEBA epoxy resin (Lin et al. 1997) cured with diamines. An aliphatic amine-curing agent, polyoxypropylene diamine (POPDA), with different molecular weights was used to cure the blends. The major peak was due to the heat generated by the normal curing reaction between POPDA and epoxide, and the second peak was due to the substitution reactions between N-aliphatic aromatic carbamate and urea with hydroxyl group of the epoxy.

When a thermoplastic is added to an epoxy resin, it will increase the viscosity of the system. Also the long polymer chains prevent the diffusion of epoxy and reactive group on the curing agent toward each other. In addition, the concentration of reactive species decreased with blending. As a result of the combined effects mentioned above, the heat of polymerization obtained from the dynamic scans decreased with the addition of thermoplastics. The decrease became more pronounced with the thermoplastic content in the blends (Barral et al. 1999; Fernandez et al. 2001; Lopez et al. 2001; Benito and Esteban 2005; Mounif et al. 2009). However the decrease in ΔH_{tot} for polycarbonate (PC)-modified epoxy is due to the following reason: transamidation reaction between amine and carbonate which proceeds at a high rate at room temperature; the exotherm of this reaction being not included in these thermograms, the amine groups participating in the transamidation

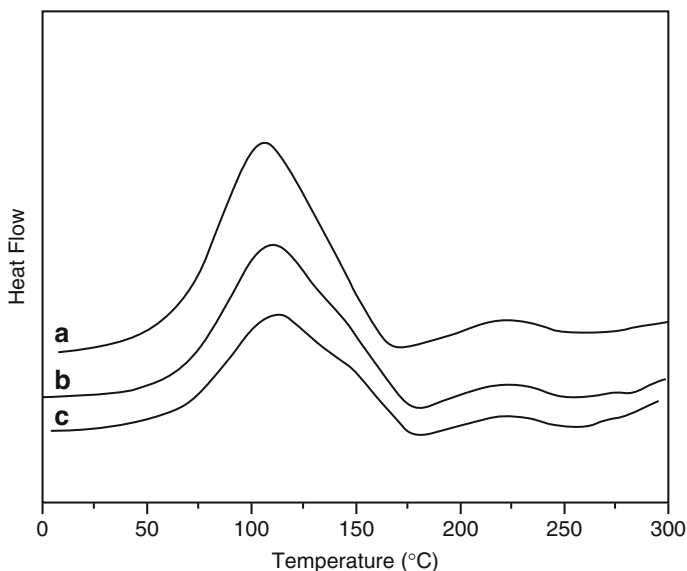


Fig. 5 Dynamic DSC runs in the temperature range between 30 °C and 300 °C (Reprinted from *J Polym Sci Part B Polym Phys* (1997) 35:2169 with permission from Wiley)

reaction does not react with oxirane, causing nonstoichiometry between oxirane and amine, and the heat of substitution reactions may be substantially lower than that of the normal curing reaction. The transamidation reaction produced phenolic hydroxyl groups which can catalyze epoxy–amine reaction. But the transamidation reaction and presence of PC dilute the system and decrease the value of the pre-exponential factor A (Lin et al. 1997). When amino-PC was used as the modifier, the amino group reacted with epoxy resin causing an increase in ΔH_{tot} and decrease in activation energy (Hao et al. 2001). When multiepoxy-terminated poly (2,6-dimethyl-1,4-phenylene oxide) was used to modify epoxy resin, ΔH_{tot} increased because of the reaction of terminal epoxy groups with the curing agent (Wang et al. 2014). The activation energy tends to increase with increase in thermoplastic in the blends. The kinetic analysis of the curing reaction in SAN/DGEBA/DDS system was performed using Kissinger and Flynn–Wall–Ozawa methods. Both the methods gave similar kinetic parameters. In this system, the activation energy showed little variation with increase in SAN in the blends (Lopez et al. 2001).

Isothermal Kinetic Analysis

The isothermal measurements of the blends and neat resin were carried out at different temperatures. The fractional conversion and rate of reaction were calculated from the heat flow against time curves. The rate of reaction, final conversion, position of peak in the isothermal curve, and area changed with isothermal cure temperature. Conventionally the isothermal curve broadened, and peak in the

isothermal curve shifted to higher cure time indicating reduced curing rate (Jenninger et al. 2000; Martinez et al. 2000; Barral et al. 2000b). But an increase in cure temperature increased the rate, final conversion, and conversion at which vitrification occurred (Fernandez et al. 2001; Zhang et al. 2009). In most of the blends, the reaction rate increased first and then decreased as the reaction progressed. This is typical of autocatalytic reactions. A representative example is DDS-cured TGDDM epoxy resin modified with polystyrene-co-acrylonitrile (SAN). The maximum conversion and rate of conversion decreased with the addition of SAN to epoxy resin. The values decreased further as more and more SAN is added to epoxy resin (Barral et al. 1999; Lopez et al. 2001).

There are exceptions to the expected behavior. In poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)-modified cyanate ester cured epoxy resin, PPO acted as a catalyst in the curing reaction resulting in a higher curing rate for the blend than neat resin in the beginning, but later the reaction rate decreased (Wu et al. 2000; Wu 2006). Due to the presence of epoxy groups, the multi-epoxy-terminated PPO increased rate of reaction than the neat resin in the early stages of curing (Wang et al. 2014). In another work, the rate of reaction increased as a result of phase separation in syndiotactic polystyrene (sPS)-modified DGEBA epoxy resin. In amine-cured system, phase separation resulted in DGEBA/MCDEA-rich phase containing some sPS and an sPS-rich phase with some dissolved DGEBA and MCDEA. In the epoxy-rich phase, the dilution and viscosity effects are negligible resulting in a faster reaction rate (Salmon et al. 2005). The presence of hydroxyl groups increased the curing rates of the blends than the neat resin in DDS-cured TGDDM/phenoxy and DGEBA/polyvinyl phenol blends (Hsieh et al. 1998; Su et al. 2005). The final cure conversion of 10 wt% PEI was found to be higher than that of neat resin until a cure temperature of 160 °C (Varley 2007; Su and Woo 1995) in an amine-cured tetrafunctional epoxy resin (Table 1). The deviation is due to the plasticization of the epoxy phase by PEI which enhanced the mobility of the epoxy network and also due to an uneven distribution of epoxide and amino species in the thermoplastic phase after RIPS.

The kinetics of the curing reactions was modeled, employing various equations described earlier. In some cases, other models were also used. Comparison of the experimental and theoretical values showed that the rate of reaction deviated from the experimental values toward the end of the reaction or at higher conversions in general. The blends showed deviation from autocatalytic behavior with increase in thermoplastic content and lowering of curing temperature and at higher conversions (Varley et al. 2000; Man et al. 2009). Toward the end of curing reaction, the viscosity of the system will increase as a result of gelation. As a consequence, the chemically controlled reaction became diffusion controlled. The increase in viscosity of the system will hinder the curing reaction, reduce the final conversion, and prevent the system from reaching full conversion. The models agreed with the experimental data with the introduction of a diffusion factor during the later stages of cure.

Reaction-induced phase separation is typical of blends of epoxy resin. Depending on the composition of the blends, dispersed or co-continuous morphology will be developed. Hence the rate of curing reaction is dependent on the phase separation

Table 1 Effect of cure temperature on the final conversion (Reprinted from *Macromol Mater Eng* (2007) 292:46 with permission from Wiley)

Cure temperature (°C)	Final conversion		
	Neat resin	10 wt% PEI	20 wt% PEI
110	0.61	0.66	0.59
120	0.65	0.73	0.96
130	0.68	0.77	0.70
140	0.73	0.80	0.65
150	0.8	0.85	0.79
160	0.88	0.87	0.85
170	0.91	0.89	0.87
180	0.97	0.96	0.89

process. As a consequence of RIPS, the curing agent and epoxy resin will be distributed in the separated phases causing a decrease in the final epoxy conversion. The MCDEA-cured DGEBA epoxy resin modified with PEI shows an interesting phenomenon. The blends showed two-phase morphology. The reaction rate at a higher PEI concentration (30 wt%) showed an increase after RIPS, whereas no sudden change was observed at 10 wt% loading of PEI. The increase in rate after phase separation results in an epoxy-amine rich phase with a faster reaction rate. In the same epoxy resin-curing agent system modified with polystyrene, the increase in rate is more pronounced due to faster phase separation (Fig. 6). In this case, the lower viscosity of the system at the initial stages of phase separation plays an important role (Bonnet et al. 1999).

The reduced reaction rate against conversion plots for phenolic-terminated PSF-modified DDS-cured TGAP is shown in Fig. 7. The parabolic shape of the curve implied a complex diffusion-controlled reaction mechanism due to higher viscosity and reduction in reactive group density (Varley et al. 2000). This phenomenon is more pronounced at higher polysulfone content (30% and 50%) and lower cure temperature (120 °C).

The activation energy of the blends calculated using the kinetic models increased with increase in thermoplastic content (Park 2009). This is because the thermoplastics hindered the curing reaction. The values of reaction orders m and n are indicators of the curing reaction. For example, in NMA-cured DGEBA epoxy resin, the value of n varied from 1.6 to 4 with increase in cure temperature and PEI content. This showed that the reaction is hindered. The value of m near 1 was similar in all cases indicating an autocatalytic mechanism (Kim et al. 2002). In the above system, the activation energy was calculated according to Arrhenius kinetics as follows:

$$r = \frac{d\alpha}{dt} = kf(\alpha) \quad (13)$$

where r is the rate of reaction, k is the apparent reaction rate coefficient, and $f(\alpha)$ is some functional dependence of rate on conversion, $\alpha(t)$. Assuming that k takes the form of an Arrhenius rate equation,

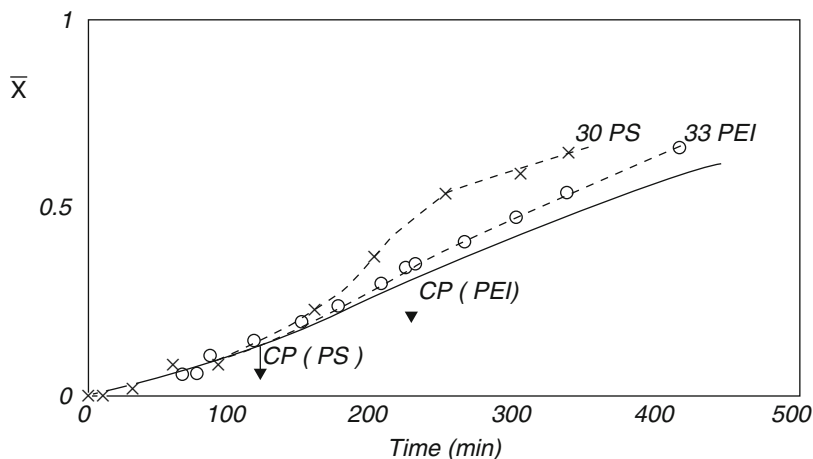


Fig. 6 Influence of the type of thermoplastic on the epoxy-amine reaction of the DGEBA–MCDEA system; experimental points for PS (×) and PEI (○) (Reprinted from *Macromolecules* (1999) 32:8517 with permission from American Chemical Society)

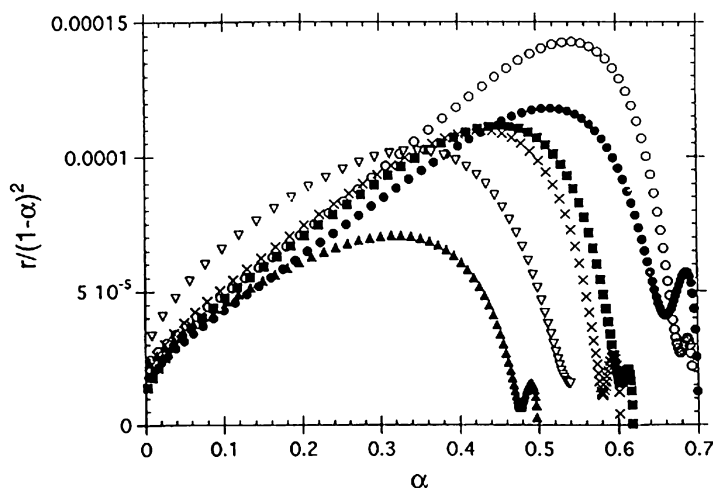


Fig. 7 Plot of the reduced rate, for $n = 2$ and $m = 1$; versus fractional cure conversion for (○) neat resin, (●) 10, (■) 15, (×) 20, (▽) 30, and (▲) 50% PSF samples during cure at 120 °C (Reprinted from *Polymer* (2000) 41:3425 with permission from Elsevier)

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (14)$$

where A is the pre-exponential factor, E_a is the apparent activation energy, and R is the real gas constant, then

$$\ln r = \ln A - \frac{E_a}{RT} + \ln f(\alpha) \quad (15)$$

By plotting $\ln r$ versus $1/T$, this equation can be used to calculate the activation energy barrier to reaction at each level of conversion without having to know accurately the function $f(\alpha)$.

The activation energy profile of a phenolic hydroxyl-terminated, polysulfone-modified TGAP cured with an amine using the above method is shown in Fig. 8. The activation energy showed large values at higher polysulfone content and at higher conversions. This shows that the curing reaction became difficult as the reaction progressed (Varley et al. 2000).

A slightly different activation energy evolution is shown in Fig. 9. The activation energy initially decreased due to the formation of hydroxyl groups which catalyzed the curing reaction, and at a later stage, it increased due to increased system viscosity. The reduction in activation energy is more for amine-terminated polyethersulfone:polyether ether sulfone copolymer (PES:PEES) than chlorine terminal PES:PEES copolymer since the amine groups reacted with epoxy resin producing more numbers of catalyzing hydroxyl groups (Man et al. 2009).

Similar activation energy profile was observed in epoxy cresol novolac resin blended with PPO, epoxide-terminated PPO with epichlorohydrin (EPPO), and multipoxy-terminated, low-molecular-weight poly(phenylene oxide) (PPOE) cured with DDS (Wang et al. 2014). The lowest activation energy was observed in PPOE system due to the presence of epoxy groups and highest in PPO-modified

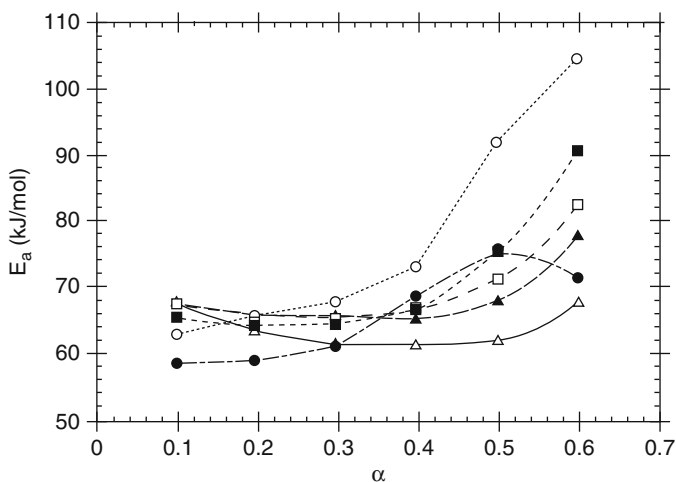


Fig. 8 Plot of activation energy versus fractional cure conversion for (Δ) neat resin, (\blacktriangle) 10, (\square) 15, (\blacksquare) 20, (\circ) 30, and (\bullet) 50% PSF samples during cure at 120 °C (Reprinted from Polymer (2000) 41:3425 with permission from Elsevier)

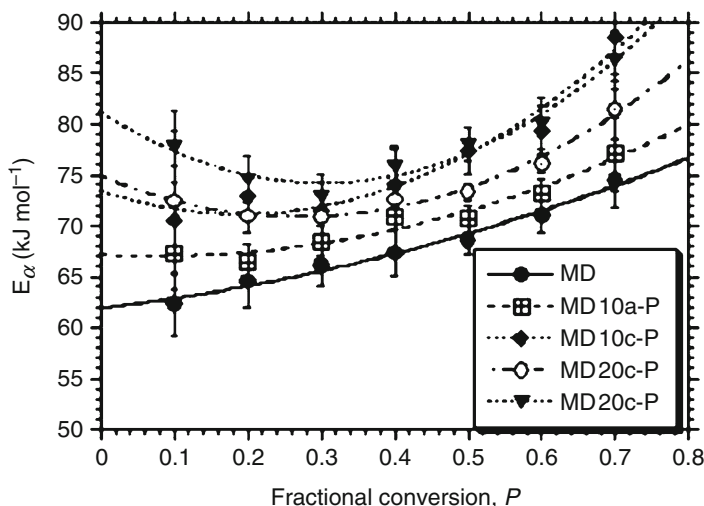


Fig. 9 The evolution of activation energy versus fractional conversion for the unmodified and modified epoxy resin system; MD10a-P and 20a-P – 10 wt% and 20 wt% amine terminal PES: PEES, MD10c-P and 20c-P – 10 wt% and 20 wt% chlorine terminal PES:PEES (Reprinted from *J App Polym Sci* (2009) 112:2391 with permission from Wiley)

system which does not contain epoxy groups. In general, the modifiers acted as catalyst at lower concentration, and at higher compositions they obstructed the curing reaction (Fig. 10).

The introduction of amine functionality on PEI altered the reaction rate versus time plot of an NMA-cured DGEBA epoxy resin (Kim et al. 2003). The plots of amino-PEI (DNCA) and PEI (DNCP) systems are shown in Fig. 11. Two peaks were observed in the DNCA system, whereas only one peak which is expected to be observed for usual thermoplastic modified epoxy resin is shown by DNCP system. The first peak in the DNCA system is attributed to the reaction between amine-terminated polyetherimide (ATPEI) with hardener/DGEBA and the second peak due to autocatalytic reaction of catalyst with hardener/DGEBA.

A modified equation was used to predict the kinetics in this case:

$$-r = \frac{d\alpha}{dt} = \sum r_i = (-r_1) + (-r_2) \quad (16)$$

where $-r_i$ is the total reaction rate and $-r_1$ and $-r_2$ are the partial reaction rates. Each reaction model can be assumed to the autocatalytic mechanism, so $-r_1$ and $-r_2$ can be written as follows:

$$-r_1 = (k_{11} + k_{12}\alpha^{m_1})(1 - \alpha)^n \quad (17)$$

$$-r_2 = (k_{21} + k_{22}\alpha^{m_2})(1 - \alpha)^n \quad (18)$$

Fig. 10 Activation energy in the non-isothermal curing processes of EPN/PPO, EPN/EPPO, and EPN/PPOE blends with different compositions (Reprinted from Polym Eng Sci (2014) 54:2595 with permission from Wiley)

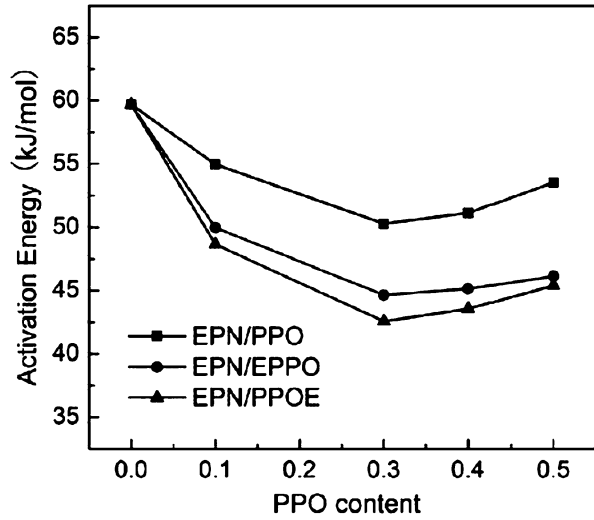
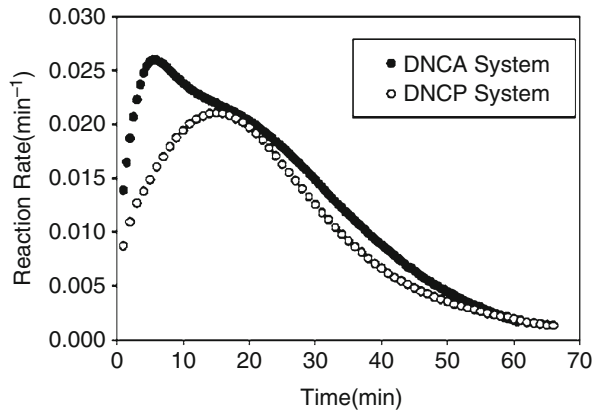


Fig. 11 Reaction rate versus time curves for the DNCP and DNCA systems at 120 °C (Reprinted from Polym Bull (2003) 51:167 with permission from Springer)



Equation 16 can be rewritten by combining the diffusion control factor, $f(\alpha)$, as follows:

$$\begin{aligned}
 -r &= \frac{d\alpha}{dt} = (k_{\alpha} + k_{12}\alpha^{m_1} + k_{22}\alpha^{m_2})(1 - \alpha)^n f(\alpha) \\
 -r &= \frac{(k_{\alpha} + k_{12}\alpha^{m_1} + k_{22}\alpha^{m_2})(1 - \alpha)^n}{1 + \exp[C(\alpha - \alpha_c)]} \quad (19)
 \end{aligned}$$

where $k_{\alpha} = k_{11} + k_{21}$.

The modified equation fits well with the experimental values as shown in the Fig. 12.

Fig. 12 Reaction rate versus degree of conversion plot for the cure process of DNCA system, experimental data (symbols) and calculated data (lines) at 140 °C (Reprinted from Polym Bull (2003) 51:167 with permission from Springer)

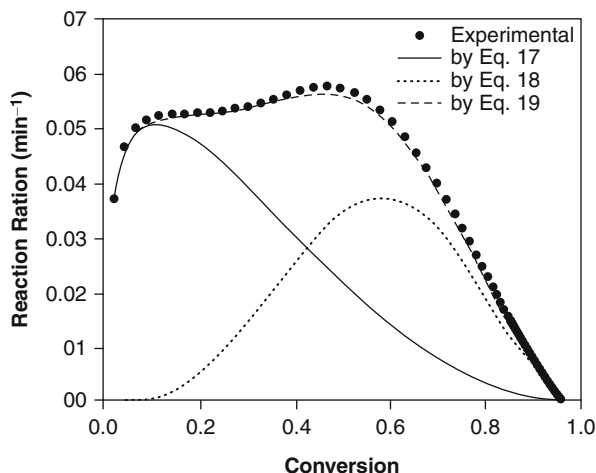


Table 2 Kinetic constants of autocatalysis models on the DNCA system (Reprinted from Polym Bull (2003) 51:167 with permission from Springer)

T (°C)	m_1	m_2	n	k_{12} (min ⁻¹)	k_{22} (min ⁻¹)
120	0.3707	3.7839	2.9677	0.0524	0.8226
130	0.3108	3.5216	2.4297	0.0889	1.2367
140	0.2735	3.0913	2.1893	0.1160	1.9263

The kinetic parameters calculated are shown in Table 2.

The values of m_1 , m_2 , and n are controlled, respectively, by the reactions of ATPEI with hardener/epoxy, catalyst with hardener/epoxy, and epoxy with hardener. The autocatalytic reaction of ATPEI was predominant in the early stages of cure due to the high activation energy of the anhydride-cured system. So m_1 was low value in the initial stages, and at the later stages, m_2 was high. The critical conversion α_c was also larger than unmodified and PEI-modified systems.

DDS-cured TGDDM/PC blends were completely miscible due to the interaction of PC with epoxy resin. As described earlier, the rate of cure reaction was higher for the blends than the neat resin. In contrary to the usual autocatalytic mechanism, the blends exhibited an n th-order reaction mechanism with n varying from 1.2 to 1.5. The model and experimental data were in good agreement till vitrification (Su et al. 1995).

Conclusions

Extensive studies have been done on the cure kinetics of thermoplastic-toughened epoxy resin. DSC is a convenient and easy-to-use technique to monitor the progress of the curing reaction. The dynamic and isothermal DSC thermograms were smooth except where there are specific interactions or side reactions. The modification with

thermoplastics did not alter the autocatalytic mechanism in general. But they influenced the final conversion and kinetic parameters due to the interaction with epoxy resin or curing agent, dilution effect, viscosity effects, and RIPS. The final conversion and the reaction rate decreased in most of the cases. The reaction rate increased in systems where the functional groups on the thermoplastic catalyzed the curing reaction. The activation energy of the epoxy-curing agent reactions also decreased in such cases. Various kinetic models were employed, and the experimental values agreed with theoretical values up to critical conversion. After critical conversion, viscosity effects dominated. After the introduction of the diffusion factor, the kinetic models agreed well with the experimental values.

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