

Reaction Kinetics of Epoxy Resin Modified with Reactive and Nonreactive Thermoplastic Copolymers

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ABSTRACT: An epoxy resin system based on a triglycidyl *p*-amino phenol (MY0510) was crosslinked using stoichiometric amounts of 4,4'-diaminodiphenyl sulfone. The epoxy was modified with random copolymers, polyethersulfone-poly(ether-ethersulfone) (PES:PEES), with either amine or chlorine end groups, at 10 and 20 wt %. The reaction kinetics for both unmodified and modified epoxy systems were studied using differential scanning calorimetry in isothermal and dynamic conditions. The results show that the degree of conversion in thermoplastic-modified epoxies at any reaction time is smaller compared with the unmodified resin. Gel point (GP) determination was done from rheological measurements. The modified system containing 20% of the PES:PEES

additive showed considerable increase in the GP. The reaction rate shows the characteristic of an autocatalytic reaction where the product acts as catalyst. The activation energy, E_a calculated from the isothermal reaction depends on the extent of conversion and increases with increasing PES:PEES content. For unmodified epoxy system, the average E_a is 67.8 ± 4.1 kJ mol⁻¹ but for systems modified with 20 wt % of amine and chlorine PES:PEES, the value increased to 74.1 ± 3.3 and 77.9 ± 4.4 kJ mol⁻¹, respectively. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2391–2400, 2009

Key words: epoxy; amine; thermoplastic; reaction rate; activation energy

INTRODUCTION

Fully reacted epoxy resins possess good thermal stability, chemical resistance, and excellent mechanical properties¹ which make them suitable for numerous applications including aerospace, automotive, appliances, construction, electrical, and furniture industries. However, the high level of crosslinking in the epoxy network often leads to brittleness.² The incorporation of a thermoplastic polymer, which is initially miscible with the reactants but phase separates during epoxy/amine reaction, has been used as a technique to improve the toughness of epoxy networks.³

Various types of thermoplastics such as poly(etherimide),^{4,5} polycarbonate,⁶ poly(ethersulfone), PES^{4,7} have been used to improve the mechanical properties of epoxy resin. Recently, a novel copolymer, polyethersulfone:polyether-ethersulfone (PES:PEES), has been blended with different epoxy resins

such as tetraglycidyl-4,4'-diaminodiphenylmethane⁸ and novalac resin.⁹ Both have been reacted with the aromatic amine 4,4'-diaminodiphenylsulfone (DDS) at the stoichiometric ratio, and also for $a/e = r = 0.77$ ($a/e =$ ratio of amino hydrogen to epoxide group) which means an excess of epoxy in the mixture. The use of PES:PEES in the epoxy resin has been reported to improve the glass transition temperature, increase the toughness, and reduce the water absorption. In another study,¹⁰ the reaction rate of PES:PEES modified epoxy resins was reported to be essentially the same as the neat resin. The epoxy system used was diglycidyl ether of bisphenol A, reacted either with methylene bis(2,6-diethylaniline) or 3,3'-DDS at the stoichiometry ratio, $r = 0.77$. However, the epoxy resin prepared in the stoichiometric ratio of $r = 0.77$ would not produce a material suitable for high performance applications. For such applications, a high glass transition temperature and modulus are desired and a stoichiometry ratio of amine/epoxy close to 1 ($r \rightarrow 1$) is necessary.

Besides the stoichiometric ratio of the reactants, the mechanical properties of the thermoplastic-modified epoxy resins are also determined by the extent of cure or chemical conversion of epoxy resin.¹¹ The other factors that influence the physical characteristics of an epoxy resin are the aromatic content, crosslink density, and the type of curing agent.¹² The degree of conversion (p) of an epoxy resin refers to

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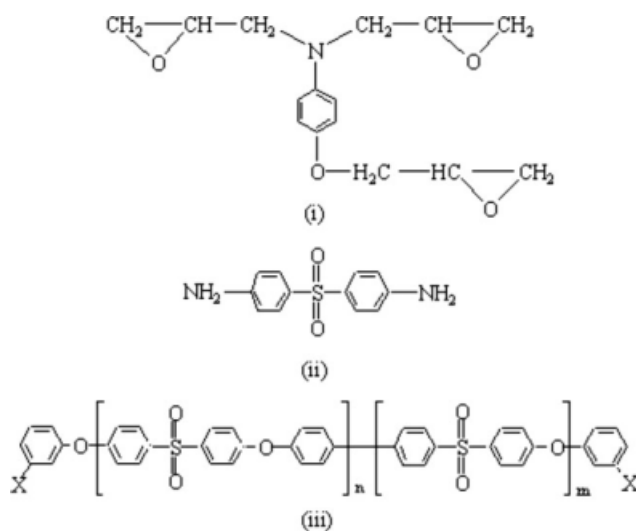


Figure 1 Structures of the materials used in this study: (i) a triglycidyl *p*-amino phenol (MY0510), (ii) 4,4'-diaminodiphenyl sulfone (DDS), and (iii) polyethersulfone-poly(ether-ethersulfone) (PES:PEES) terminated with amine ($X = \text{NH}_2$) or chlorine ($X = \text{Cl}$) groups.

the extent of crosslinking that has advanced throughout the polymer network. Maximum conversion is necessary to minimize the presence of unreacted reactive groups, which can cause network defects and consequently introduce structural weaknesses in the cured resin.¹³ The available literatures shows that thermoplastic modifiers with reactive chain-ends greatly influence the morphologies.^{14,15} Different morphologies are produced as a result of reaction of active chain-ends of the thermoplastic with the epoxide groups to form interpenetrating polymer network. The incorporation of a thermoplastic into epoxy-amine resins may alter the cure kinetics and reaction mechanism and consequently the degree of conversion. Kinetic behavior of epoxy resins is fundamental to understand the structure-property-processing relationship for manufacture and application of high performance composites. Reliable information of the reaction kinetics of these materials is also essential in modeling their processing. Therefore, a knowledge of the effects of a particular thermoplastic in an epoxy-amine blends—such as the rate of reaction, final conversion, and activation energy—is essential to predict and control the end properties of the cured materials.

In the above context, it is pertinent to study the conversion and kinetics of unmodified and modified epoxy reactions over practical ranges of the process parameters. In this work, we have investigated the effect of amine (reactive) or chlorine (nonreactive) endgroups of PES:PEES on the reaction kinetic and the gel point (GP) of the MY0510/DDS epoxy system (Fig. 1) reacted at the stoichiometry ratio, $r = 1$. Isothermal and dynamic (temperature-scan mode)

experiments were conducted to obtain the information of chemical conversion. For measuring the activation energy, E_a , a model based on isothermal differential scanning calorimeter (DSC) curing that did not require knowledge of reaction rate equation was used. It was assumed that for a given degree of conversion, the reaction process has the same mechanism of reaction, regardless of the temperature.

Evaluation of kinetic parameters: Theoretical principles

The reaction kinetics of epoxy resins has been widely studied using the DSC.^{16–18} The basic assumption of this procedure is that the heat flow relative to the instrumental base line is proportional to the reaction rate. It is further assumed that the temperature gradient within the sample and the temperature difference between the sample and reference are small.¹⁹ A simple theory of kinetic study and evaluation of the activation energy is outlined here following Lu and Kim,¹⁶ Fu et al.,¹⁷ and Ramirez et al.¹⁸

The reaction rate, dp/dt , at a given temperature is assumed to be a function of the degree of conversion, $f(p)$. The basic equation for the lumped kinetics can be written as:

$$\frac{dp}{dt} = kf(p) \quad (1)$$

where the degree of conversion at any time (t) during *isothermal* reaction is denoted by $p = \Delta H_t / \Delta H_c$ [ΔH_t = heat of reaction at time t , and ΔH_c = heat of complete reaction] and k = the “rate constant.” In this approach, the reaction mechanism is assumed to remain unchanged as the reaction proceeds and eq. (1) maintains the same form regardless of temperature. Integrating eq. (1) over a reaction time t with corresponding conversion p , we have

$$kt = \int [1/f(p)] dp = \varphi(p) \quad (2)$$

Equation (2) shows that the rate constant k is inversely proportional to time for a given p regardless of the functional form of $f(p)$ at a given temperature.

The dependency of the reaction rate constant on temperature follows the Arrhenius law:

$$k = k_0 e^{\frac{-E_a}{RT}} \quad (3)$$

Substituting eq. (3) in eq. (2) and taking logarithms on both sides, yields the following

$$\ln t = \frac{E_a}{RT} + A \quad (4)$$

where E_a is the activation energy (kJ mol^{-1}), A is a constant which is the difference between the

logarithm of $\varphi(p)$ of eq. (4) and the logarithm of the frequency factor k_0 , and R is the gas constant ($8.315 \text{ J K}^{-1} \text{ mol}^{-1}$). From eq. (4), it appears that a plot of the logarithm of the time needed to reach a fixed conversion p versus the inverse of reaction temperature, $1/T$ should be linear with a slope E_a/R . This equation was used to calculate the activation energy of the reaction of the unmodified and modified epoxy systems.

EXPERIMENTAL

Materials and methods

The epoxy prepolymer used in this work was a triglycidyl *p*-amino phenol (MY0510), supplied by Ciba-Geigy Co., United Kingdom, with an epoxy equivalent weight of $101.8 \pm 1.2 \text{ g eq}^{-1}$. To determine the equivalent weight, 0.3 g of an epoxy prepolymer was dissolved in 50 mL dichloromethane and 10 mL of TEAB reagent (25% *w/v* solution of tetraethyl ammonium bromide in glacial acetic acid). The solution was then titrated against standard perchloric acid solution using methyl violet as the indicator.²⁰ The curing agent was 4,4'-DDS, supplied by Aldrich, having a molar mass of 248 g mol^{-1} and purity above 98%. The two thermoplastics used were random copolymers of PES:PEES terminated with amine ($M_n = 12,100 \text{ g mol}^{-1}$) or chlorine ($14,400 \text{ g mol}^{-1}$) groups, were received from ICI Ltd., United Kingdom. The molecular structures of the materials used in this study are shown in Figure 1. Samples were prepared without using any solvent. For an unmodified system (MD), the MY0510 and DDS were mixed in a rotary evaporator at 150°C . A mixing time of 3 min was sufficient to get a clear homogeneous solution. A different technique was used for modified epoxy systems. For these systems, 10 and 20 wt % of amine or chlorine terminated PES:PEES were mixed with MY0510 at 180°C in a rotary evaporator to get a clear solution. The curing agent (DDS) was separately melted in an aluminum container at 190°C . The clear solution of PES:PEES/epoxy mixture was then blended with molten DDS at 190°C and mixed for 40 s to get a uniform and clear mixture. The extent of reaction during sample preparation could not be measured. However, the kinetic studies with the samples (to be described later) indicated that the conversion in the mixing stage was limited to a maximum of 3%. Each mixture was quenched immediately with liquid nitrogen to stop the reaction and was stored at -28°C . The amine/epoxy stoichiometric ratio was held constant at $r = 1.0$, for all epoxy systems. The coding of the samples of the unmodified and modified MY0510/DDS systems are shown in Table I.

TABLE I
Sample Codes and Composition of the Unmodified and Modified MY0510/DDS Systems

Sample codes	Sample	Composition (wt %)
MD	MY 0510/DDS	62.15/37.85
MD10a-P	MY 0510/DDS/NH ₂ -PES:PEES	55.95/34.05/10
MD20a-P	MY 0510/DDS/NH ₂ -PES:PEES	49.7/30.3/20
MD10c-P	MY 0510/DDS/Cl-PES:PEES	55.95/34.05/10
MD20c-P	MY 0510/DDS/Cl-PES:PEES	49.7/30.3/20

Fourier transform infrared spectrophotometric analysis

The reactivities of amine-terminated PES:PEES with the epoxy prepolymer was studied using Fourier transform infrared spectrophotometry (FTIR). Infrared spectra were collected on a Nicolet Impact 410 FTIR spectrophotometer. Omnic software (Nicolet Instrument Corp.) was used for all data acquisition and subsequent data analysis. A thin film of amine- and chlorine-terminated PES:PEES copolymers was prepared by casting a solution of the polymer in dichloromethane onto a NaCl plate at room temperature. Most of the solvent was allowed to evaporate at room temperature, and final drying of the sample was done in a vacuum oven at 60°C for 3 h. The sample on a NaCl plate was then placed inside the FTIR-temperature chamber directly mounted in the spectrometer. This unit was driven by an Eurotherm 071 temperature controller. Before the measurement was carried out, the FTIR-temperature chamber was calibrated with a contact thermocouple. The reaction temperature was maintained at $180 \pm 0.5^\circ\text{C}$ and the FTIR spectra were obtained from 16 scans at a resolution of 4 cm^{-1} . Similar steps were followed for the preparation of a thin film of 50/50 wt % of amine-terminated PES:PEES/ MY0510 mixture for reactivity analysis.

Differential scanning calorimetry

Measurements were conducted on a TA Instrument DSC 2920 calibrated with high purity indium standards. Dry nitrogen was used as the purge gas; the flow rate was 50 mL min^{-1} . The characterization of unmodified and modified epoxy resins was carried out in the dynamic temperature-scan mode²¹ to obtain the heat of complete reaction, ΔH_c , and the kinetic parameters. The value of ΔH_c , which is associated with the complete chemical conversion ($p = 1$) of all the reactive groups, was calculated from the average of five DSC temperature-scan experiments from -80 to 350°C using different heating rates of 2, 5, 10, 15, and $20^\circ\text{C min}^{-1}$.^{19,22} Isothermal reaction for both the unmodified and modified epoxy systems

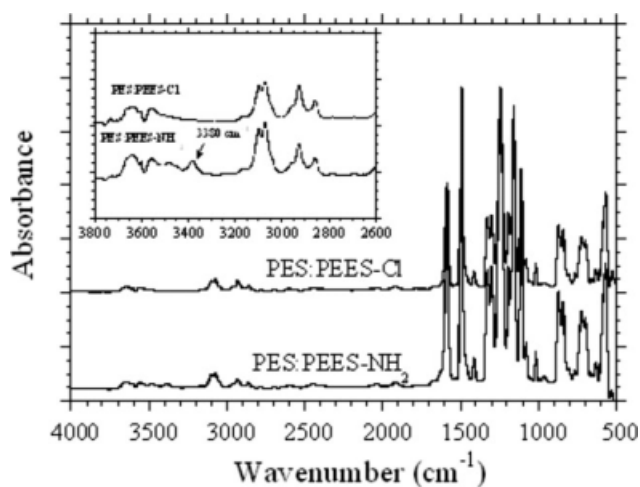


Figure 2 FTIR spectra of amine- and chlorine-terminated PES:PEES in the range of 4000–600 cm^{-1} wave number with inset of close up spectra in the region of 3800–2600 cm^{-1} .

was conducted in the temperature range of 140–190°C to obtain the extent of reaction or degree of conversion.

Temperature-modulated differential scanning calorimetry

In this study, the glass transition temperature, T_g , were carried out using temperature-modulated differential scanning calorimetry (TMDSC) measurements after isothermal analysis. The tests were performed using the TA Instrument DSC 2920, operating under modulated mode. First, the sample was reacted under isothermal temperature 180°C in the DSC pan, and then was cooled to –50°C at a rate of 20°C min^{-1} followed by scanning using a modulated heating program at 5°C min^{-1} to 340°C to determine the T_g . The amplitude was 2°C, and a period of 60 s. The calorimetric scans were performed with nitrogen gas flowing at a rate of 50 $\text{cm}^3 \text{min}^{-1}$.

Rheological analysis

The rheological technique involved an isothermal multiwave test based on Fourier transform response to a multifrequency wave. The technique was used to determine the GP. A Rheometrics Mechanical Spectrometer (RMS-800) operating at a strain of 2.5% was used for small amplitude oscillatory shear measurements. A sample of 0.5-mm thickness held between a pair of disposable parallel plates, 50 mm in diameter, was used for the measurement of storage shear modulus (G') and the loss shear modulus (G'') at seven frequencies (0.25, 1, 2, 4, 8, 16, and 32 Hz) and 180°C.

RESULTS AND DISCUSSION

The coupling of reactive thermoplastic with the epoxy and the subsequent development of morphology may influence the reaction kinetics. It is therefore, important to obtain direct evidence of the reactions between the reactive thermoplastic and the epoxy resin. In addition, studies were carried out to determine whether the curing time and the temperature used are adequate for the reaction to occur. The characteristics of the reaction mass were monitored primarily by FTIR. The FTIR spectra of both amine- and chlorine-terminated PES:PEES in the mid-IR region are shown in Figure 2 and the band assignments^{23,24} are summarized in Table II. As it appears from Figure 2, the absorption peaks of both copolymer are almost similar. A closer examination of the amine-terminated PES:PEES spectrum, however, indicates the presence of a primary amine at 3380 cm^{-1} as shown in the inset. This peak was used to monitor the reaction of epoxide group of MY0510 with the amine end group PES:PEES.

The depletion of the primary amine was estimated by measuring the decrease in peak height of the primary amine band at wavenumber 3380 cm^{-1} at time, t and calculated using the following expression:

$$\text{Percent residual (NH}_2\text{--)} \text{ at time, } t = \left(\frac{(A_{3380}/A_{1591})_t}{(A_{3380}/A_{1591})_0} \right) \times 100 \quad (5)$$

where A_{1591} is the absorbance of the phenylene group at 1591 cm^{-1} and was used as the internal standard. The suffix 0 in the denominator indicates that the quantity is evaluated at zero time.

Figure 3(a) shows the decrease in the primary amine peak height measured at 3380 cm^{-1} of PES:PEES/epoxy mixture with the reaction time. The depletion of primary amine calculated using eq. (5) is illustrated in Figure 3(b). The plot shows that at 180°C, about 90% of primary amine was depleted within 1 h. This results clearly indicate that the amine end group of PES:PEES is reactive enough to be grafted to the epoxy chains during the preparation and curing stages.

TABLE II
Peak or Band Assignments for PES:PEES

Peak or band (cm^{-1})	Assignment
3450 – 3250 s	$\nu(\text{NH}_2)$
1591 s	$\nu(\text{C}=\text{C})$ Aromatic bands
1497 w	$\nu(\text{C}=\text{C})$ Aromatic bands
1295 s	$\nu(\text{Ar}-\text{O}-\text{C})$
1280 s	$\delta(-\text{SO}_2-)$ sulfone bands
1151 s	$\delta(-\text{SO}_2-)$ sulfone bands
1110 w	$\delta(-\text{SO}_2-)$ sulfone bands

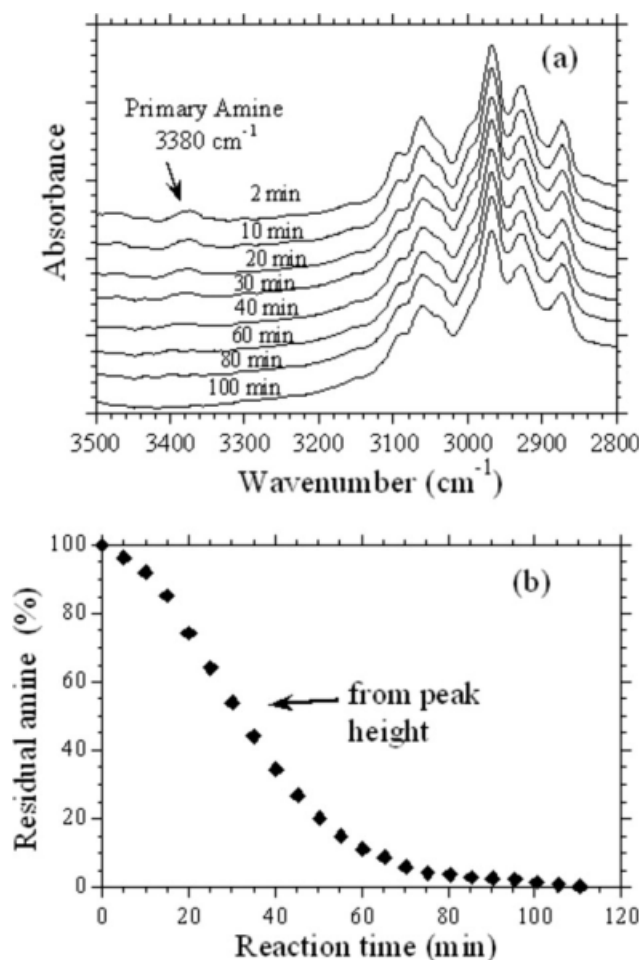


Figure 3 (a) FTIR spectroscopy data (mid-IR region) for modified epoxy resin reacting at 180°C and (b) depletion of primary amine of PES:PEES blends calculated using eq. (5).

Dynamic temperature-scan mode MD using DSC

The average ΔH_c values obtained from five different heating rates on unmodified MD systems are shown in Table III. The heat of polymerization per mol of epoxide (ΔH_{polym}) was also calculated. The ΔH_{polym} of MD systems was found to be 100.0 kJ mol⁻¹, which is in good agreement with reported values in the range of 90–110 kJ mol⁻¹.¹¹ A similar calculation was applied to all modified MD systems, and the results of ΔH_c , ΔH_{polym} , and the maximum peak exo-

TABLE III
Average Values (Mean \pm SD) for ΔH_c , ΔH_{polym} , and the Exothermic Peak Temperature, T_p , of the Unmodified and Modified Epoxy Systems

System	ΔH_c /J g ⁻¹	ΔH_{polym} (kJ mol ⁻¹ epoxy)	T_p /°C
MD	611 \pm 12	100.3 \pm 2.4	216 \pm 1
MD10a-P	524 \pm 13	95.5 \pm 2.4	222 \pm 1
MD20a-P	478 \pm 15	98.1 \pm 3.0	231 \pm 2
MD10c-P	538 \pm 12	98.0 \pm 2.1	223 \pm 2
MD20c-P	466 \pm 14	95.6 \pm 2.9	228 \pm 3

therm temperature T_p , are presented in Table III. As expected, within experimental error ΔH_c decreased linearly with increasing thermoplastic content, and no significant deviations from simple additivity were observed.

Apart from the ΔH_c value, the temperature-scan mode can also provide useful preliminary information on the reaction kinetics of the epoxy systems. The effect of incorporating PES:PEES is indicated by a shift of the maximum peak exotherm temperature, T_p , to a higher temperature as the fraction of PES:PEES was increased. Representative DSC traces of the unmodified and modified MD systems are shown in Figure 4. The exothermic peak temperature, T_p , in temperature-scan mode provides a qualitative measurement of the reaction rate for a given heating rate. Jayle et al.²⁵ observed that T_p decreased with increasing polycarbonate loading in the diglycidyl ether of bisphenol A/4,4'-diamino diphenyl methane (DGEBA/DDM) system. They attributed this to the increase in the epoxy cure reaction. The reaction behavior of epoxy prepolymers with varying chain lengths reacted with DDS was investigated by Gonis et al.²⁶ They found that as the epoxy chain length was increased, T_p also increased with simultaneous decrease in the ΔH_c . The increase in T_p was related to the slower polymerisation rate due to a lower reactivity of longer epoxy prepolymer chain. From Table III, it can be seen that T_p increases (about 3–8°C) with increasing loading of PES:PEES in the epoxy resins. Thus, it can be inferred that incorporation of amine- or chlorine-terminated PES:PEES in the MD systems, lowered the reaction rate to some extent.

Figure 5 shows the reaction rate, dp/dt , versus time, t , calculated from the isothermal results at 190°C for the unmodified and modified MD systems.

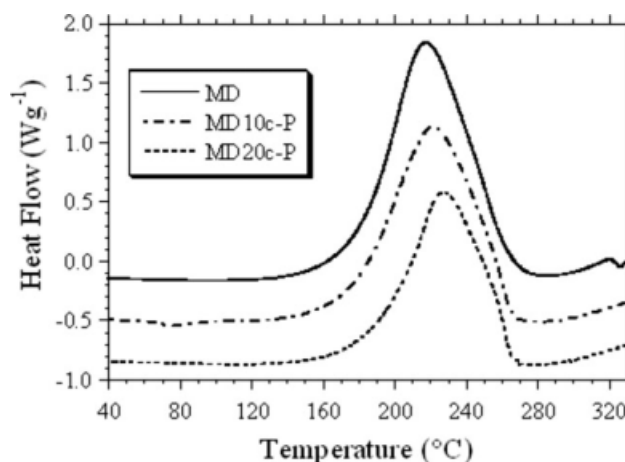


Figure 4 Representative DSC curves of unmodified and modified MD with chlorine-terminated PES:PEES systems. Curves have been shifted for clarity: ordinate scale refers to MD system.

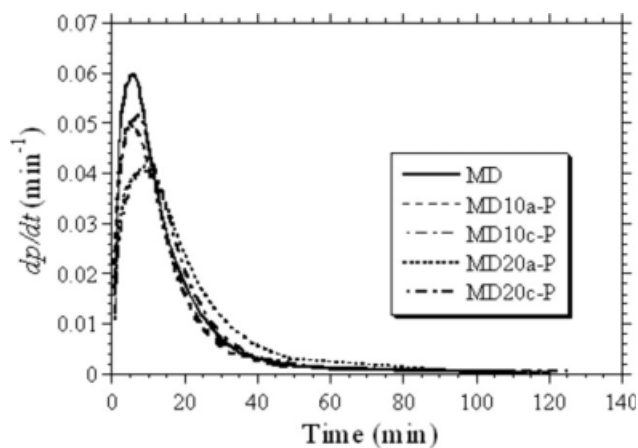


Figure 5 The plot of reaction rate versus reaction time for the unmodified and modified MD systems, reacted isothermally at 180°C.

It can be observed that the nature of the reactions were typically autocatalytic in all cases, with the maximum rate of conversion being achieved soon after the start of the reaction. The reaction rates were affected by the presence of PES:PEES; the rate decreased as the PES:PEES content were increased.

Isothermal reaction kinetics of unmodified and modified MD systems

The change in conversion with reaction time for the isothermal reaction of the MD system is presented in Figure 6. It is seen that the conversion increased with increasing reaction temperature. Analogous results were obtained with MD10a-P, MD20a-P, MD10c-P, and MD20c-P systems. The conversion was next plotted against $\ln t$ and the resulting curves for the reaction at different constant temperatures for the unmodified and modified MD systems are shown in Figure 7(a,b), respectively. All the curves

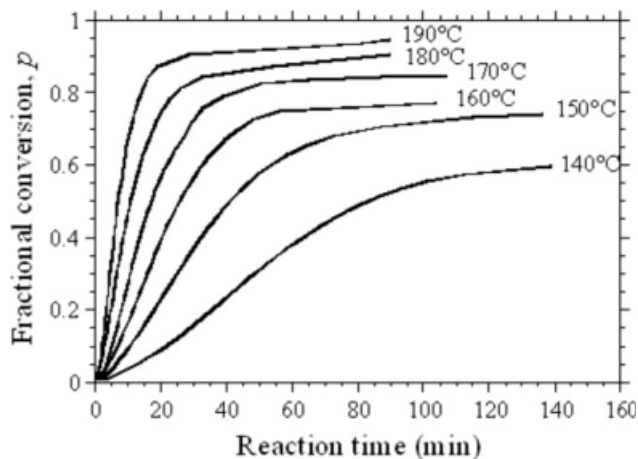


Figure 6 Plots of fractional conversion, p versus reaction time for the unmodified MD system at different isothermal reaction temperatures.

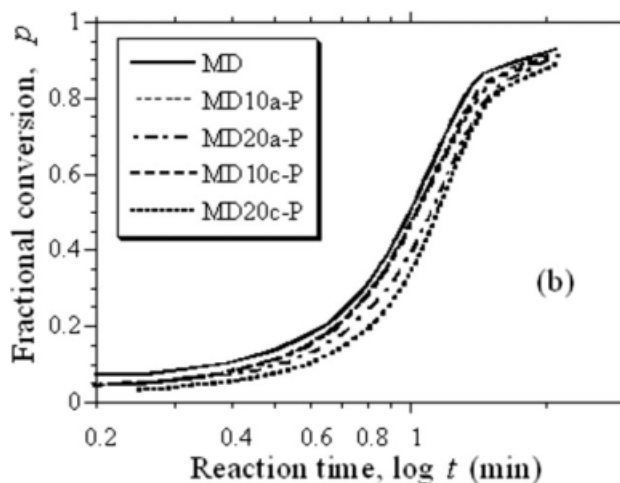
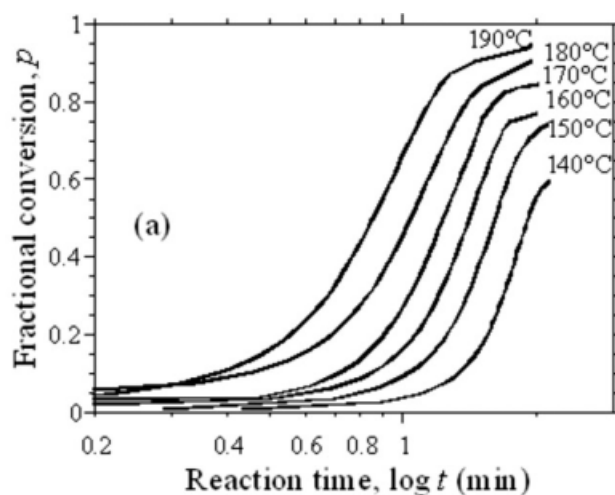


Figure 7 Plots of fractional conversion, p versus $\log t$ (time) for (a) the unmodified MD system reacted isothermally at different temperatures and (b) modified MD systems reacted isothermally at 180°C.

have the same shape but were shifted along the time axis for different cure temperatures. In addition, the slopes of these curves are nearly the same over the intermediate range of conversion, suggesting that the same overall cure mechanism prevailed in the temperature range investigated in this study. Also, from Figure 7(a,b), it is easy to estimate that the conversion at the stage of sample preparation remained limited to a maximum of 3% as stated before.

However, a slight difference in the initial reaction was observed for the curves at 190°C and that at 180°C. This was due to some measurement loss since the reaction at 190°C was too vigorous. Some of the reaction heat might have been released before it was detected by the calorimeter. The incorporation of PES:PEES in the MD system resulted in a reduction of the reaction rate, and consequently the final conversion was decreased. The presence of a modifier is suspected to have some dilution effect on the system that might have reduced the chances of the reactive

TABLE IV
Maximum Conversion at T_c (the Reaction Time where the Curves Converge to the Base Line) and T_g of the Unmodified and Modified MD Systems from Isothermal Reaction at 180°C

System	Conversion (%)	T_g (at T_c) (°C)
MD	93 ± 2	210 ± 1
MD10a-P	91 ± 2	194 ± 1
MD20a-P	90 ± 2	193 ± 1
MD10c-P	90 ± 2	191 ± 1
MD20a-P	87 ± 2	184 ± 1

epoxy and amine to react. For a comparison of the final conversions, the results from the isothermal analysis at 180°C for the amine-terminated and chlorine-terminated PES:PEES systems are summarized in Table IV. The final conversion is taken at the time where the curve stabilized and reached the base line. The glass transition temperatures of the cured products at respective maximum conversions are also given in Table IV. The T_g of a cured product could not be measured after isothermal reaction since the exothermic peak observed in the DSC curves, arising out of residual reaction between the epoxy monomer and DDS, overlapped with the changes in the specific heat capacity, C_p , at glass transition. Therefore, TMDSC was used in this study to measure the T_g after isothermal reaction. The overall results show that the T_g 's of epoxy phase of modified systems are lower than the unmodified MD system. The difference can be related to the lower conversion attained after isothermal reaction at 180°C. Other factors, such as plastisizing effect due to unreacted PES:PEES polymer chains and flexibiliser effect from the formation of copolymer of amine-terminated PES:PEES with the network structure, may reduce the T_g .²⁷

GP determination

Determination of the GP in course of development of a polymer network is very important in the processing of thermosets since beyond the GP the polymer loses its liquid property and ability to flow. The GP was determined from the plot of $\tan \delta$ ($\delta = G''/G'$) versus frequency where they exhibit congruence, $G' \propto G''$. The GP also corresponds to parallel lines in a log (modulus) versus log (frequency) plot.^{28,29} The log-log plots of the "loss tangent" ($\tan \delta$) against frequency for the unmodified system is shown in Figure 8(a). The plots of G' and G'' against the frequency are presented in Figure 8(b). Figure 8(a) shows that the crosslinking reaction of the unmodified system (MD) occurred very rapidly at 180°C and the measurements taken at different frequencies were not obtained at the same reaction time. Figure 8(b) indicates that the plots of G' and G'' do not coin-

cide at 10.1 min but the G' line which was below the G'' line at that time, partially crosses the latter at 10.6 min. Hence, the GP is estimated at 10.1 ± 0.5 min. Blending with 10 wt % amine- or chlorine-terminated PES:PEES (MD 10a-P and MD10c-P) did not show any appreciable change in the GP. However, the modified systems MD 20a-P and MD20c-P that contained 20 wt % of the additive showed considerable increase in the GP from 10.1 ± 0.5 to 13.1 ± 0.6 and 12.1 ± 0.6 min, respectively [Fig. 9(a,b)]. The GPs of the blends of different recipes are given in Table V.

Determination of the activation energy (E_a)

The time needed to attain different degrees of conversion was determined from isothermal reaction using DSC at different temperatures. For a particular degree of conversion, it is possible to correlate the logarithm of curing time with the inverse of the temperature by using eq. (4). Figure 10 shows the plot of $\ln t$ versus $1/T_c$ for the unmodified system. For

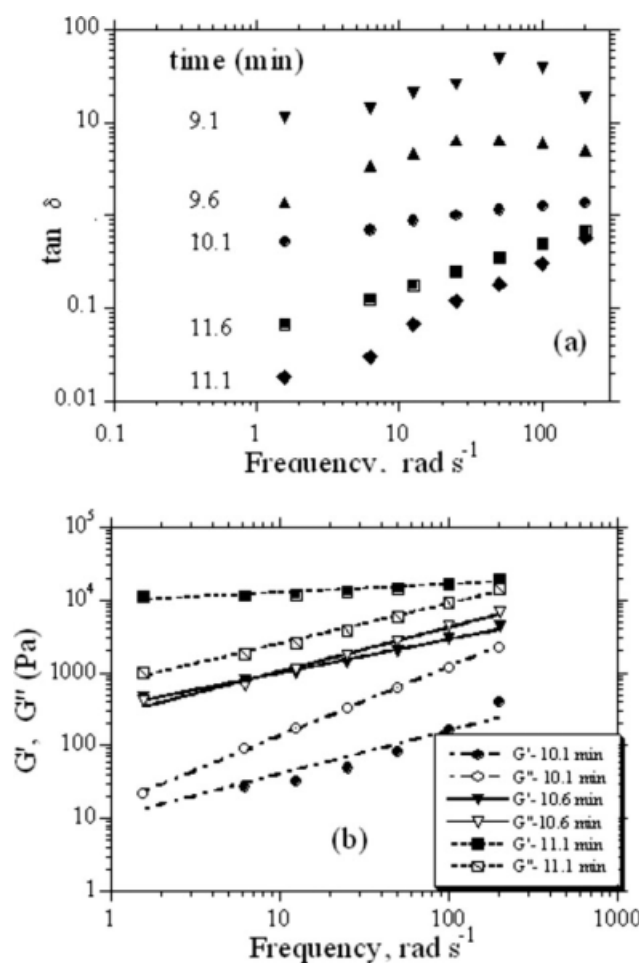


Figure 8 Log-log plots of (a) $\tan \delta$ versus frequency and (b) storage shear modulus G' , and loss shear modulus G'' versus frequency of the unmodified MD system at 180°C.

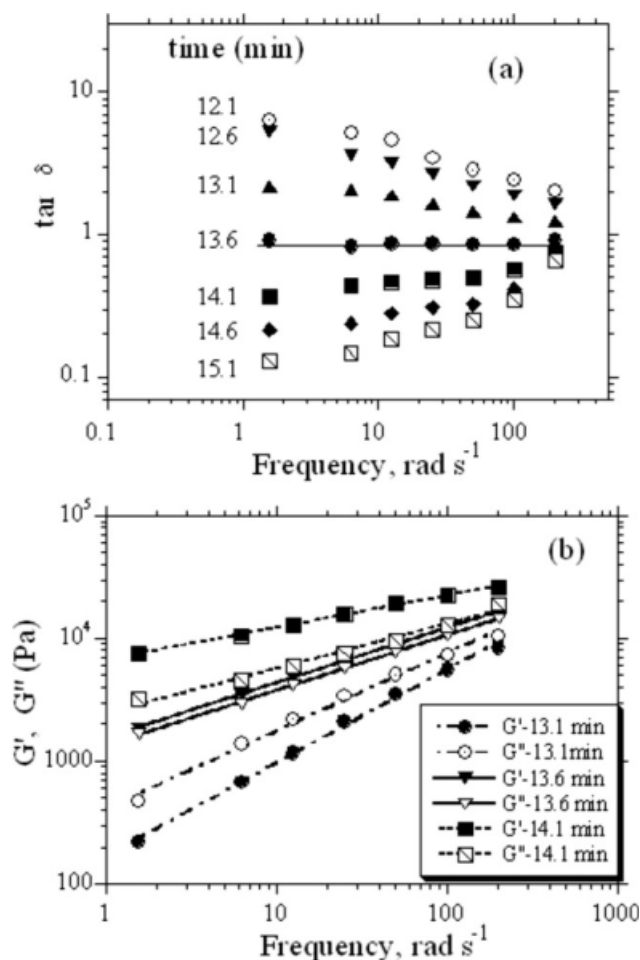


Figure 9 Log-log plots of (a) loss tangent ($\tan \delta$) versus frequency and (b) storage shear modulus G' , and loss shear modulus G'' versus frequency for the MD20a-P at 180°C .

each degree of conversion, the value of the activation energy can be obtained from the slope of the corresponding straight line. A set of straight lines were obtained for different constant values of the conversion (p). Similar calculations were performed for the modified systems also. The plots of E_a against conversion, p , for both unmodified and modified samples are shown in Figure 11. It appears that the values of the activation energies were not constant. The activation energies for all unmodified and modified systems at the beginning of the reaction (10%

TABLE V
Values of Gel Time Obtained from Rheological Analysis for the Unmodified and Modified MD Systems at 180°C

System	$t_{\text{gel}}/\text{min}$
MD	10.1 ± 0.5
MD10a-P	10.7 ± 0.8
MD20a-P	13.1 ± 0.6
MD10c-P	10.3 ± 0.5
MD20c-P	12.1 ± 0.6

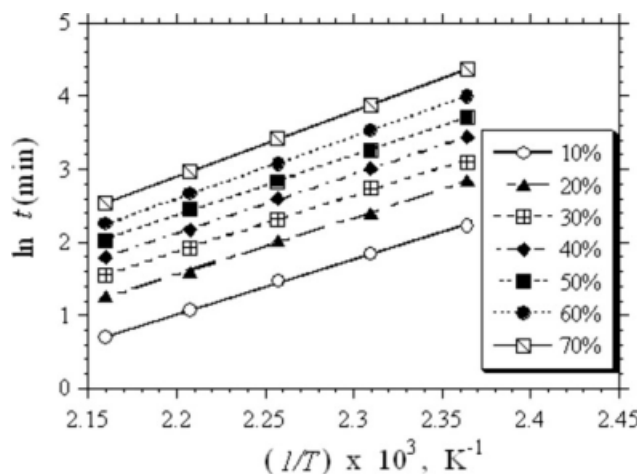


Figure 10 Correlation of logarithm of reaction time versus the inverse of the reaction temperature for different conversions of the unmodified MD system.

conversion) were lower than the activation energy at 70% conversion. Between 10 and 70% conversion, the E_a changed and reached a minimum value at 20% conversion for chlorine-terminated modified system (MD20c-P) and at 30% for the amine-terminated modified systems (MD20a-P). After 60% conversion, the E_a increased rather rapidly. The average activation energy for the unmodified MD system is $67.8 \pm 4.1 \text{ kJ mol}^{-1}$. The average activation energy, E_a of both kinds of systems in the conversion range of 10–70% are given in Table VI.

For the MD system, the activation energy increases monotonically with the degree of conversion (Fig. 11). The phenomenon expectedly occurs because of a simultaneous increase in the viscosity of the reaction mixture and its deterring effect on the mobility of the reactant molecules or segments. The activation energy for a modified system shows an initial decrease followed by gradual increase. As

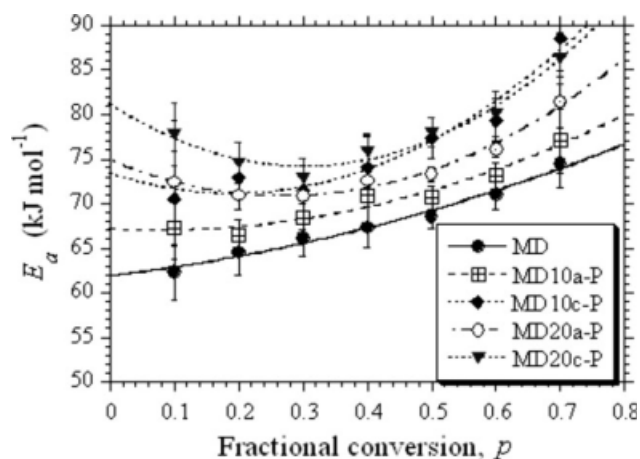


Figure 11 The evolution of activation energy, E_a versus fractional conversion for the unmodified and modified MD systems.

TABLE VI
Activation Energies, E_a , at Different Degrees of Conversion for the Unmodified and Modified MD Systems

Conversion (%)	$E_a/\text{kJ mol}^{-1}$				
	MD	MD10a-P	MD20a-P	MD10c-P	MD20c-P
10	62.4	67.3	72.4	70.5	77.8
20	64.5	66.4	71.0	72.9	74.6
30	66.1	68.5	70.9	71.5	72.9
40	67.4	70.8	72.6	74.0	75.8
50	68.6	70.7	73.3	77.4	78.0
60	71.0	73.2	76.1	79.3	80.1
70	74.5	77.1	81.4	88.6	86.3
Average	67.8	70.8	74.1	76.2	77.9
SD	4.1	3.8	3.7	6.3	4.4

the reaction proceeds, hydroxyl groups are formed from the reaction between the amine and the epoxy prepolymer. The hydroxyl groups facilitate ring opening and thereby catalyzes the curing reaction. This is accompanied by a reduction in the activation energy.¹⁷ However, the production of hydroxyl groups declines and the viscosity of the medium goes up as the conversion increases. This gives rise to an increase in the activation energy as in the case of an unmodified system. A similar trend in variation of activation energy of epoxy systems has been amply reported in the literature. For example, an increase in the activation energy at conversion above 50% was observed by Gonis et al.²⁶ for a difunctional epoxy system, and by Salla and Ramis³⁰ for a polyester resin. Barton³¹ made a similar observation for a tetrafunctional-diamine system at above 70% conversion. A comparison between the amine and chlorine-terminated PES:PEES shows that the amine (reactive end group) gave a lower activation energy. This is in conformity with the above explanation of the pattern of change of the activation energy since the chlorine end groups, which are nonreactive, do not generate hydroxyl groups and cannot have any conducive effect on activation energy.

CONCLUSIONS

The kinetic effects caused by the presence of a random copolymer, PES:PEES, in the reaction of an epoxy-amine have been studied. In general, the incorporation of either amine- or chlorine-terminated PES:PEES in the MD systems reduces the reaction rate due to dilution effect, and reduces the chain mobility due to increased viscosity. Complete conversion cannot be obtained over the reaction time used in this study due to topological restrictions. The results show that the degree of conversion in thermoplastic-modified epoxies for any given reaction time is smaller compared with the unmodified resins. No large difference in the degree of conver-

sion between the amine- or chlorine-terminated PES:PEES modified systems was observed. As a result, the T_g of the modified systems are lower than the unmodified MD system. The incorporation of PES:PEES delayed the GP. Addition of 20 wt % of amine- and chlorine-terminated PES:PEES increased the GP from 10.1 ± 0.5 to 13.1 ± 0.6 and 12.1 ± 0.6 min, respectively. The reaction mechanism of the epoxy blends remained the same as that of the unmodified epoxy systems. The activation energy, E_a calculated from the isothermal reaction depends on the extent of conversion and increases with increasing PES:PEES content. A rapid increase in E_a was observed after 50–60% of chemical conversion which can be attributed to the increase in viscosity of the system due to gelation. The average activation energy E_a for unmodified epoxy system is 67.8 ± 4.1 kJ mol^{-1} . When blended with 20 wt % of amine and chlorine PES:PEES, the activation energy of each blend increased to 74.1 ± 3.3 and 77.9 ± 4.4 kJ mol^{-1} , respectively.

References

1. Ellis, B. In *Chemistry and Technology of Epoxy Resins*; Ellis, B., Ed.; Blackie Academic: Glasgow, 1993.
2. Lee, W. H. *Polymer Blends and Alloys*; Folkes, M. J.; Hope, P. S., Eds. Blackie Academic: Glasgow, 1993.
3. Mimura, K.; Ito, H.; Fujioka, H. *Polymer* 2000, 41, 4451.
4. Bonnaud, L.; Pascault, J. P.; Satereau, H. *Eur Polym J* 2000, 36, 1313.
5. Barral, L.; Cano, J.; Lopez, J.; Lopez-Bueno, I.; Nogueira, P.; Torres, A.; Ramirez, C.; Abad, M. J. *Thermochim Acta* 2000, 344, 127.
6. Su, C. C.; Woo, E. M. *J Polym Sci Part B: Polym Phys* 1997, 35, 2141.
7. Park, S. J.; Li, K.; Jin, F. L. *J Ind Eng Chem* 2005, 11, 720.
8. Blanco, I.; Cicala, G.; Faro, C. L.; Recca, A. *J Appl Polym Sci* 2003, 89, 268.
9. Blanco, I.; Cicala, G.; Costa, M.; Recca, A. *J Appl Polym Sci* 2006, 100, 4880.
10. Blanco, I.; Cicala, G.; Motta, O.; Recca, A. *J Appl Polym Sci* 2004, 94, 361.
11. Rozenberg, B. A. In *Advances in Polymer Science*; Dusek, K., Ed. Springer-Verlag: Berlin, 1986.

12. Hourston, D. J.; Lane, J. M.; Zhang, H. X. *Polym Int* 1997, 42, 349.
13. Kim, B. S.; Chiba, T.; Inoue, T. *Polymer* 1995, 36, 43.
14. MacKinnon, A. J.; Jenkins, S. D.; McGail, P. T.; Pethrick, R. A. *Polymer* 1993, 34, 3252.
15. Cicala, G.; Spina, R. L.; Recca, A.; Sturiale, S. *J Appl Polym Sci* 2006, 101, 250.
16. Lu, M.; Kim, S. *J Appl Polym Sci* 1999, 71, 2401.
17. Fu, T.; Zhang, G.; Zhong, S.; Zhao, C.; Shao, K.; Wang, L.; Na, H. *J Appl Polym Sci* 2007, 105, 2611.
18. Ramirez, C.; Rico, M.; Lopez, J.; Montero, B.; Montes, R. *J Appl Polym Sci* 2007, 103, 1759.
19. Barton, J. M. In *Advances in Polymer Science*; Dusek, K., Ed. Springer-Verlag: Berlin, 1985; Vol. 72.
20. Lee, H.; Neville, K. *Handbook of Epoxy Resins*; Mc Graw-Hill: New York, 1967; Chapter 1.
21. Stefani, P. M.; Moschiar, S. M.; Aranguren, M. I. *J Appl Polym Sci* 2001, 79, 1771.
22. Barton, J. M. *Polymer* 1980, 21, 603.
23. Schiraldi, A.; Baldini, P.; Samanni, G.; Gardenal, M. *J Therm Anal* 1984, 29, 645.
24. Colthup, N. B. In *Encyclopedia of Physical Science and Technology*; Mayer, R. A., Ed. Academic Press: Orlando, 1987; Vol. 6.
25. Jayle, L.; Bucknall, C. B.; Partridge, I. I.; Hay, J. N.; Fernyhough, A.; Nozue, I. *Polymer* 1996, 37, 1897.
26. Gonis, J.; Simon, G. P.; Cook, W. D. *J Appl Polym Sci* 1999, 72, 147.
27. Shaw, S. J. In *Additive and Modifiers for Epoxy Resins in Chemistry and Technology of Epoxy Resins*; Ellis, B., Ed. Blackie Academic: Glasgow, 1993; Chapter 4.
28. Winter, H. H.; Morganelli, P.; Chambon, F. *Macromolecules* 1988, 21, 532.
29. Matejka, L. *Polym Bull* 1991, 26, 109.
30. Salla, J. M.; Ramis, X. *J Appl Polym Sci* 1994, 51, 453.
31. Barton, J. M. *Br Polym J* 1986, 18, 37.