

# Rheokinetic cure characterization of epoxy–anhydride polymer system with shape memory characteristics

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**Abstract** An epoxy resin capable of exhibiting shape memory property was derived by curing diglycidyl ether of bisphenol A (DGEBA) with a blend of carboxy telechelic poly(tetramethyleneoxide) (PTAC) and pyromellitic dianhydride (PMDA). The cure kinetics of DGEBA/PTAC/PMDA blend of varying compositions was investigated using isothermal rheological analysis. The overall reaction conformed to a second-order autocatalytic model. The kinetic parameters including reaction order, kinetic constants and activation energy were determined. The results showed that increase of PTAC decreased the overall activation energy and frequency factor of the cure reaction. This effect resulted in a diminution of the overall rate of curing. The catalysis by PTAC has its origin from the activation of epoxy groups by the protons of the COOH groups. The autocatalysis was caused by the COOH groups generated by the reaction of alcohol groups with anhydride. The activation energy for the autocatalysis was more than that for the primary reaction as the COOH groups responsible for autocatalysis were generated on a sterically hindered polymer backbone. The kinetics helped generate a master equation conforming to second-order autocatalytic

model that could predict the cure profile of a specified resin system at a given temperature, leading to cure optimization.

**Keywords** Shape memory polymer · Epoxy resin · Poly(tetramethyleneoxide) · Rheokinetics

## Introduction

A shape memory material has the ability to remember its permanent shape after deformation into a temporary shape, while the temporary shape remains stable even after the stress responsible for the deformation is released. External stimuli, such as temperature, pH, light, etc., are required for a deformed shape-memory material to recover its original stress-free state [1]. The driving force for shape recovery in a polymer is the elastic strain generated during the deformation. Shape memory polymers have shown great promises for a wide range of applications, such as actuators, self-deployable systems, etc. [2].

Shape memory epoxy (SMEP) resins generally possess excellent shape memory performance with high shape retention, shape recovery, rapid response and unique thermal and mechanical properties. The tensile strength, storage modulus and thermal transition temperature of SMEP can be easily tuned in a large range by varying the formulation. Besides, SMEP has superior environmental durability, which makes it a good candidate for space applications [3]. Our approach to derive SMEP is to incorporate poly(tetramethyleneoxide) (PTMO) segment in polymer matrix as this group confers shape memory property to the system. This strategy has been adopted by us in realization of shape memory epoxy resin [4], polyurethane [5] and acrylic system in an earlier study [6]. With a view to derive shape memory epoxy matrix with better

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flexibility characteristics and lower  $T_g$ , an anhydride was chosen as the curative for epoxy resin while, a carboxy-terminated PTMO polymer was used as a co-curative. In this study, 30–60 mass percentage of PTAC was retained in the blend, so that it shows meaningful shape memory property. Since PTAC contains COOH groups capable of reacting with epoxy groups, the anhydride concentration is chosen such that concentration of carboxyl and anhydride together equals that of the epoxy groups. This makes the relative concentration of PMDA vary from compositions to composition. PTAC can alter the kinetics of the epoxy–anhydride reaction by way of its interaction with the epoxy groups. It is of interest to investigate the related kinetics by rheometry. The ultimate objective is to derive the conditions for the optimum curing of the resin at different loading of PTAC in the matrix.

The effect of anhydride structure on the cure kinetics and thermal stability of a tetrafunctional epoxy resin has been reported [7]. In another study, the low temperature curing behaviour of an epoxy–anhydride mixture was studied by means of vibrational FT-Raman spectroscopy under isothermal conditions [8]. It was observed that at low temperatures and in the absence of catalyst, the autocatalysis of anhydride is less prominent. Earlier investigations of epoxy–anhydride reaction using different techniques such as gel permeation chromatography [9], nuclear magnetic resonance [10], vibrational spectroscopy [11] and DSC [12, 13] principally examine the kinetics of the reaction in presence of tertiary amine as catalyst. In majority of the cases, the reaction conformed to first-order kinetics. There have not been any studies on the kinetics of epoxy–anhydride reaction co-cured by a carboxylic acid. This article investigates the kinetics of epoxy–anhydride reaction in presence of carboxy-terminated PTMO (i.e. PTAC). PTAC was chosen so that the resultant polymer could potentially show shape memory properties.

## Experimental

### Materials

Hydroxy telechelic PTMO with an average molecular mass  $M_n = 2,000$  g/mol was supplied by Aldrich Chemicals, USA. Maleic anhydride (CDH chemicals, Mumbai, India) was purified by sublimation. Epoxy resin, diglycidyl ether of bisphenol A (DGEBA) with an epoxy value 5.4 eq/kg, was procured from Ciba Geigy, India. Its equivalent mass was determined by chemical analysis. Triethylamine (TEA), tetrahydrofuran (THF), and toluene (all supplied by SRL chemicals, Mumbai, India) were purified by distillation. PTMO and epoxy resin were dried in flash evaporator at 80 °C for 5 h before use. Pyromellitic dianhydride

(PMDA) (Koch-Light Laboratories Ltd, England) was dried in vacuum oven at 80 °C for 3 h.

### Synthesis of carboxy telechelic PTMO (PTAC)

PTAC was synthesized by reaction of PTMO with maleic anhydride in THF in the presence of TEA as catalyst. PTMO (0.1 mol) was added slowly to maleic anhydride (0.4 mol) in THF kept at room temperature. After the addition, the mixture was refluxed for 16 h, and the solvent was removed by distillation. The resultant viscous fluid was dissolved in toluene and washed several times with distilled water to remove traces of the TEA and unreacted maleic anhydride. The toluene solution was dried over  $\text{Na}_2\text{SO}_4$  for 1 day, filtered and the solvent was removed in a flash evaporator for 6 h at 80 °C. The resultant resin was characterized by Fourier transform infrared spectroscopy (FTIR) and size exclusion chromatography (SEC). Estimation of COOH content was done by chemical analysis.

### Preparation of DGEBA–PTAC–PMDA thermoset system

Initially, DGEBA was thoroughly mixed with PTAC. Then, PMDA was gradually added to the blend with constant stirring. The resin system was evacuated. Blends with different mass percentages of DGEBA/PTAC/PMDA were prepared following the same procedure. The compositions are given in Table 1.

### Characterization

FTIR spectra were recorded on a Perkin-Elmer spectrum GXA at a resolution of  $4\text{ cm}^{-1}$ . The SEC was carried out using Waters alliance 2690 separation module in conjunction with Waters 410 differential refractive index detectors and UV detectors. The columns were Waters HR1 and HR2 Styragel columns.

### Rheological analysis

Rheological characterization was done using a Reologica Stresstech Rheometer, model Reologica Viscotech QC

**Table 1** Composition of the blend system

Ref. No.	Equivalent ratio of components <sup>a</sup> DGEBA/PTAC/PMDA	Mass% of components, DGEBA/PTAC/PMDA
PTEP-1	1/0.07/0.88	59/25/16
PTEP-2	1/0.10/0.90	52/34/14
PTEP-3	1/0.16/0.92	44/44/12

<sup>a</sup>DGEBA—difunctional, PTAC—difunctional, PMDA—tetrafunctional

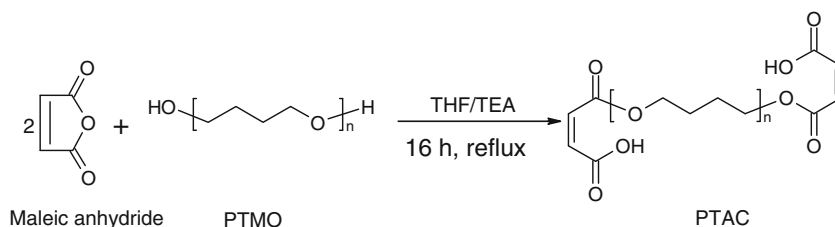
using 20-mm parallel plate assembly in oscillation mode at a frequency of 1 Hz and controlled strain of 1%. The gap between the plates was maintained at 0.7 mm. The samples were loaded onto the plates at 50 °C. The isothermal experiments were done by measuring the dynamic modulus ( $G'$ ) at different time intervals for different temperatures (160, 165, 170 and 175 °C). The data analyses were done using the instrumental software.

## Results and discussion

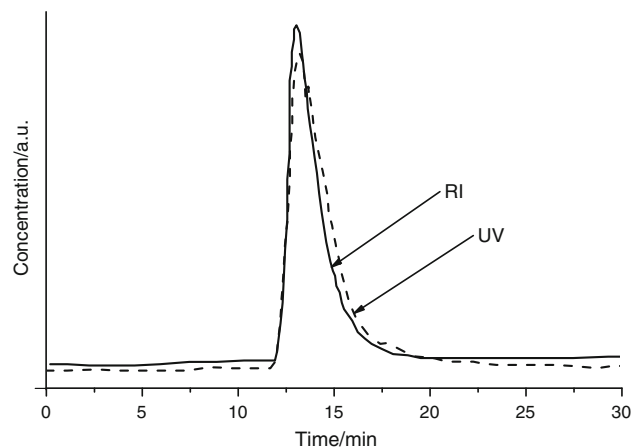
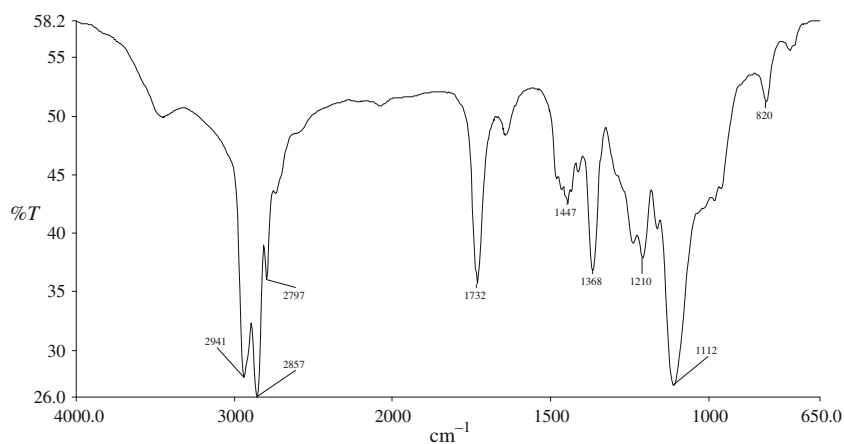
### Synthesis and characterization of PTAC

The synthesis of PTAC is illustrated in Scheme 1 and the FTIR spectrum of PTAC is shown in Fig. 1. The peak at  $3,454\text{ cm}^{-1}$  corresponds to vibration of  $-\text{OH}$  groups present in COOH group and that at  $1,732\text{ cm}^{-1}$  corresponds to  $\text{C}=\text{O}$  stretching due to ester group. The peak at  $1,110\text{ cm}^{-1}$  corresponds to  $\text{C}-\text{O}-\text{C}$  stretching. The polymer is further characterized by acid value estimation. The acid value of PTAC (49 mg KOH/g) nearly conformed to the theoretical value (52 mg KOH/g). Figure 2 presents the SEC spectra of PTAC. PTMO is insensitive to UV detector as it does not contain any chromophoric groups. On end-capping with COOH group, it becomes a UV sensitive. The similarity in SEC profiles by both refractive index and UV detector technique shows that all polymer chain ends are end-capped with COOH groups.

**Scheme 1** Synthesis of PTAC



**Fig. 1** FTIR spectrum of PTAC

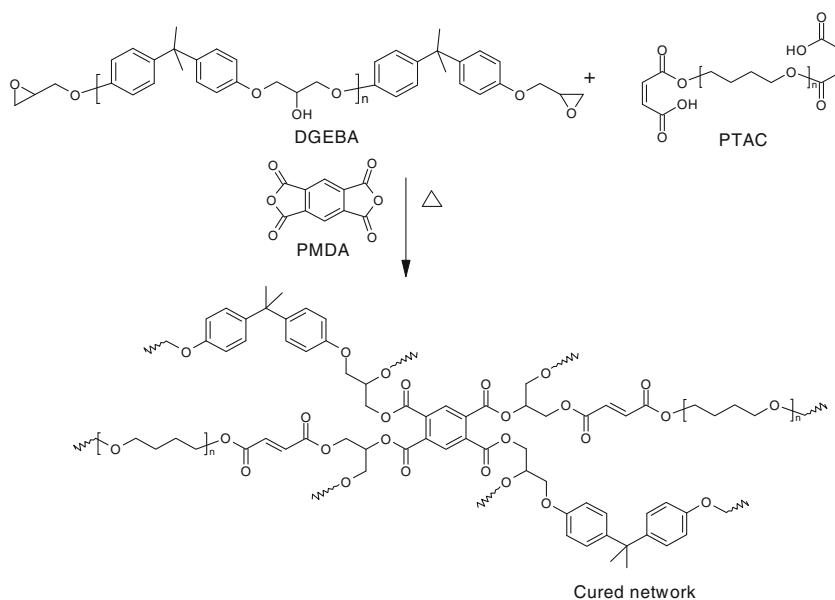


**Fig. 2** SEC profiles of PTAC (superimposition of RI and UV detected traces)

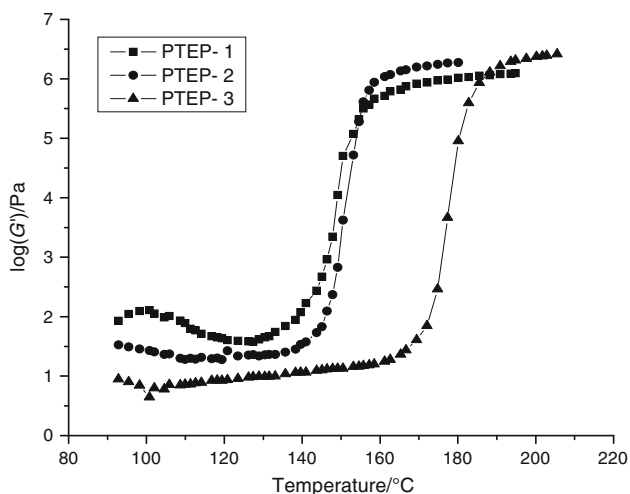
### Cure kinetics

The likely cure reaction of an ideal system of DGEBA/PTAC/PMDA blend at high temperature is illustrated in Scheme 2. The possible reactions are (i) epoxy ring opening by the carboxyl groups of PTAC followed by (ii) the reaction of epoxy groups with anhydride in PMDA [14, 15]. In the blend composition care is taken to see that anhydride and acid put together equals to epoxy groups. Figure 3 shows the non-isothermal cure profiles of various compositions of DGEBA/PTAC/PMDA blend. The modulus increases continuously and attains a plateau region as

**Scheme 2** Cure reaction for an ideal blend of DGEBA/PTAC/PMDA (hypothetical ratio 1:1:1)



the cure is completed. The plateau of storage modulus graph is more or less in the same temperature range for all compositions. On increasing the concentration of PTAC, the gelation point shifts to higher temperature scale. Thus, PTEP-3 with the higher concentration of PTAC shows a significant shift of the storage modulus to high temperature region. This shows that the cure reaction becomes less facile on increasing the PTAC content. This is attributed to the replacement of difunctional PTAC by the tetrafunctional and more reactive dianhydride. Figure 4 depicts the evolution of storage modulus as a function of time at isothermal temperatures 160, 165, 170 and 175 °C for the typical blend PTEP-1. The storage modulus attains a maximum and follows a plateau after a certain time interval, which is considered as the time for cure

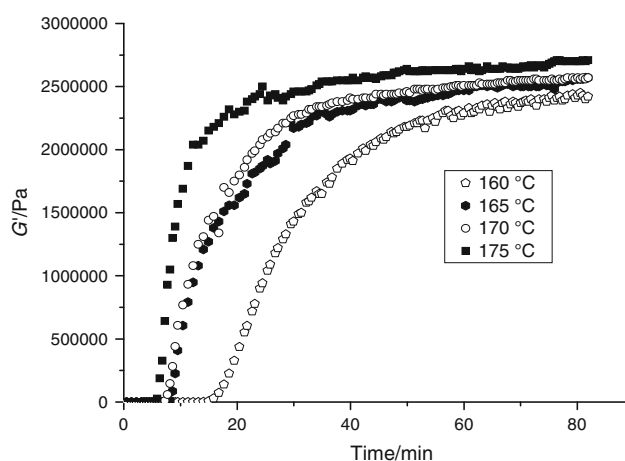


**Fig. 3** Storage modulus as a function of temperature for different composition of DGEBA/PTAC/PMDA blend (temperature range 50–250 °C, heating rate—3 °C min<sup>-1</sup>; 1 Hz)

completion. With increase in cure temperature, the modulus increases while the cure time decreases. The apparent rheological fractional conversion at any time is calculated using Eq. 1.

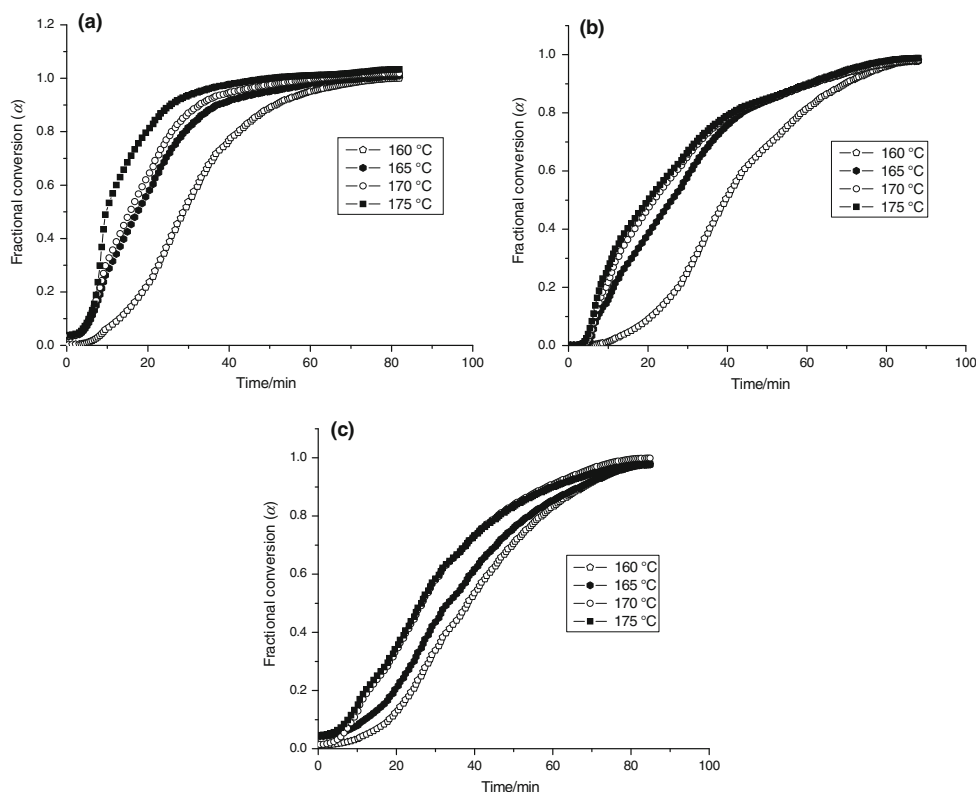
$$\alpha = \frac{G'(t)}{G'(\alpha)} \quad (1)$$

where  $G'(t)$  is the storage modulus at time  $t$ ,  $G'(\alpha)$  is the maximum modulus at each temperature. The resultant time–fractional conversion profiles for varying compositions are depicted in Fig. 5a–c. It can be observed that the fractional conversion shows a rapid increase after the gelation is triggered. The steep increase in reaction rate is indicative of the possible autocatalytic nature of the cure mechanism. The apparent fractional conversion at a given time decreases with increase in PTAC content in the blend.



**Fig. 4** Storage modulus as a function of time at different isothermal temperature for PTEP-1

**Fig. 5** Isothermal fractional conversion as a function of time at different isothermal temperatures for **a** PTEP-1, **b** PTEP-2 and **c** PTEP-3



For example, at 170 °C, conversion occurred to an extent of 64, 49 and 35% within 20 min for PTEP-1, PTEP-2 and PTEP-3, respectively.

Figure 6a–c depict the rate of fractional conversion as a function of time at different isothermal temperatures for the three systems. This is done by the differentiation of the time–conversion graph. The initial increase in rate again implies the autocatalytic nature of the reaction. At a given time, the rate of reaction gradually decreases with increase in percentage of PTAC. This is attributed to the replacement of tetrafunctional anhydride by the difunctional PTAC.

In general, the kinetics models of thermosetting resins fall into two main types: *n*th-order model and autocatalytic model. For an *n*th-order kinetics model, the following equation is applicable.

$$d\alpha/dt = k(1 - \alpha)^n \tag{2}$$

However, this model can, in general be applied to the earlier stage of the curing reaction of thermosetting resins. The experimental data were fitted with different kinetic models whereby it was found that the data (rate of fractional conversion versus apparent rheological fractional conversion) conformed best to an *n*th-order autocatalytic model [16]. For such a case, the rate of fractional conversion ( $d\alpha/dt$ ) and the extent of reaction ( $\alpha$ ), are related to one another as follows:

$$d\alpha/dt = (k_1 + k_2\alpha^m)(1 - \alpha)^n \tag{3}$$

where *m* and *n* are the kinetic exponents of the reaction and their sum represents the overall reaction order.  $k_1$  and  $k_2$  are the primary and autocatalytic reaction rate constants, respectively. The primary reaction ( $k_1$ ) corresponds to the epoxy group with the anhydride (promoted by COOH groups). The COOH groups generated by way of reaction of the –OH groups with the anhydride can catalyse the epoxy–anhydride reaction accelerating for the autocatalysis ( $k_2$ ). The OH groups can be either present in DGEBA or impurity or can be generated by way of reaction with PTAC. The rate constants follow Arrhenius temperature dependence, as given in Eq. 4.

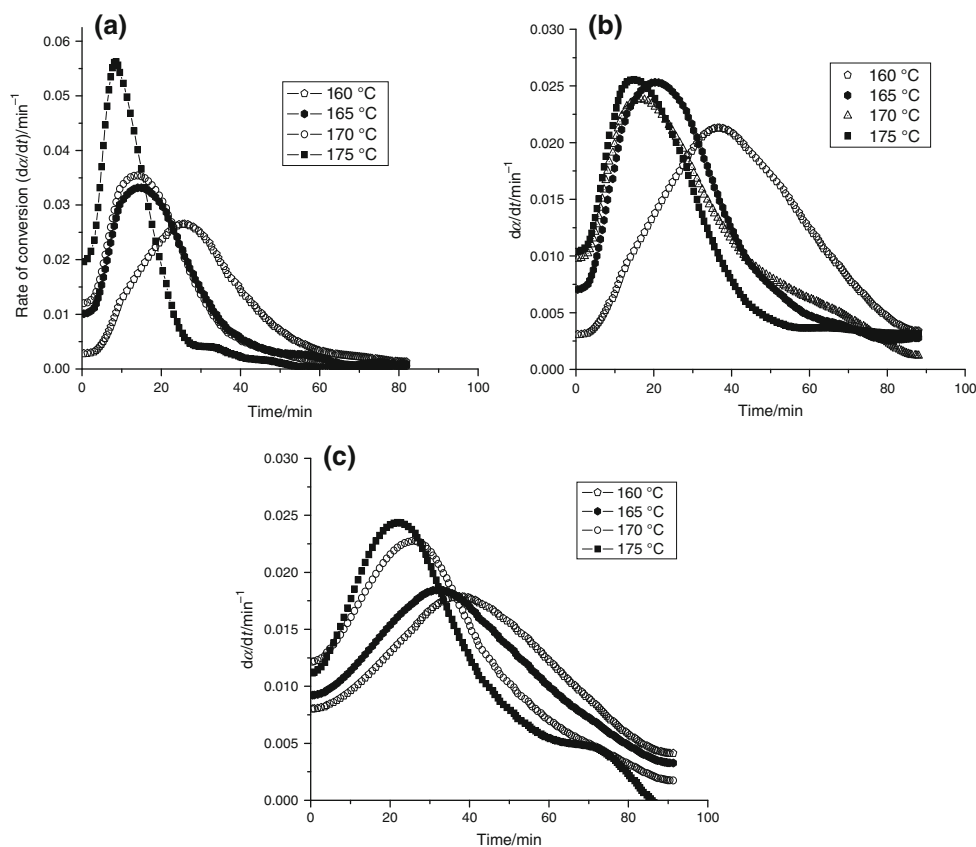
$$k_i = A_i e^{(-E_i/RT)}, \quad i = 1, 2. \tag{4}$$

where  $A_i$  is the frequency factor,  $E_i$  the activation energy,  $R$  the gas constant and  $T$  the temperature in Kelvin.

In the present study,  $k_1$  was graphically calculated as the initial rate of conversion at the point where the curve meets the y-axis in the  $d\alpha/dt$  versus  $\alpha$  plot as shown in Fig. 7 for a typical case (PTEP-1).

The other kinetic parameters,  $k_2$ , *m* and *n*, were calculated by fitting the experimental data to Eq. 3 for each temperature by a multiple regression analysis (computer aided). Typical curve-fitting plots for the different compositions at 160 °C are shown in Fig. 8. Similar acceptable

**Fig. 6** Conversion rate as a function of time at different isothermal temperature for **a** PTEP-1, **b** PTEP-2 and **c** PTEP-3



curve fits were obtained in all cases, implying that the reaction conformed to an  $n$ th-order autocatalytic model. The kinetic parameters obtained by this method are given in Table 2. For all compositions, temperature dependence of the kinetic constants is shown in Fig. 9a, b.

The overall reaction orders were obtained by averaging the values of  $m$  and  $n$  from all the experiments. The reaction order ( $m + n$ ) converged nearly to 2. The activation energies and frequency factors, given in Table 3 for the primary and autocatalytic steps are calculated from Arrhenius relation (Eq. 4).

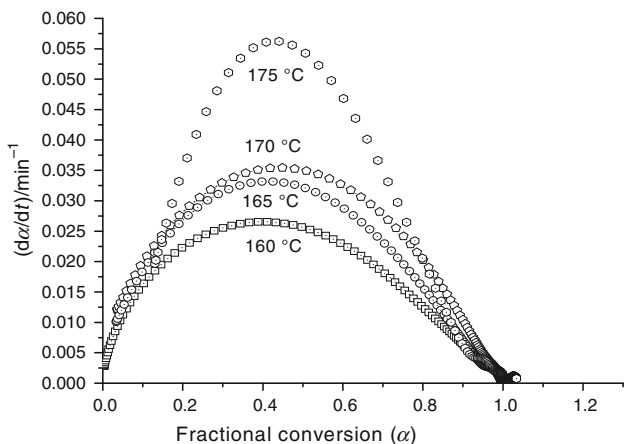
#### Effect of composition on kinetics

The rate constants  $k_1$  and  $k_2$  decrease as the composition of the blend becomes enriched in PTAC. This is caused by the fact that anhydride is more reactive than carboxylic acids of PTAC in their reaction with epoxy group. Though PTAC decreases the overall activation energy, this advantage is found to be offset by a larger decrease in frequency factor, diminishing the effective rate constants. From PTEP-1 to PTEP-3 there is a systematic increase in concentration of PTAC at the cost of concentration of PMDA. Part of the epoxy groups gets opened by the COOH terminal of epoxy resin (Scheme 3). Thus, a change in cure mechanism also

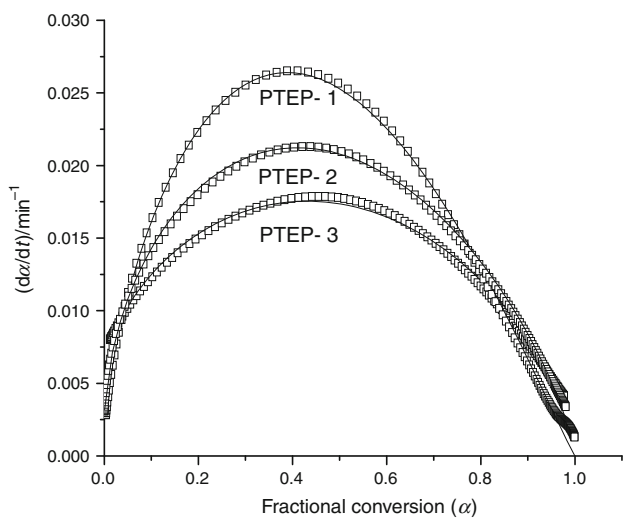
accounts for the overall decrease in rate constants with increase in concentration of PTAC. Hydrogen bonding of the  $-\text{COOH}$  group with the anhydride in the transition state could promote ring-opening of anhydride group by the epoxy groups. The COOH group generated from PMDA by its reaction with OH groups present in epoxy resin leads to the autocatalytic effect [8]. These COOH groups as well as those groups present in PTAC could promote the epoxy-anhydride reaction by hydrogen bonding with epoxy ring or the anhydride group (Scheme 3).

$k_1$  and  $k_2$  naturally increases with increase in temperature for a given compositions. Thus, the rate constants depend on temperature as well as composition. The activation energies decrease with increase in PTAC content because of the catalytic effect of COOH terminals as already discussed. The activation energy for the low COOH content recipe (PTEP-1) is in agreement with the values reported in other studies (FTIR, DSC) as 70–80 kJ/mole [14–16]. This variation of activation energies ( $E_1$  and  $E_2$ ) and frequency factor ( $A_1$  and  $A_2$ ) with PTAC concentration is demonstrated in Fig. 10a and b. The activation energy for autocatalytic step is more than that for the primary reaction. This is attributed to the fact that autocatalysis is shown by COOH groups generated on a polymer backbone, which is likely to manifest steric hindrance.





**Fig. 7** Conversion rate as a function of fractional conversion ( $\alpha$ ) for PTEP-1 at various temperatures



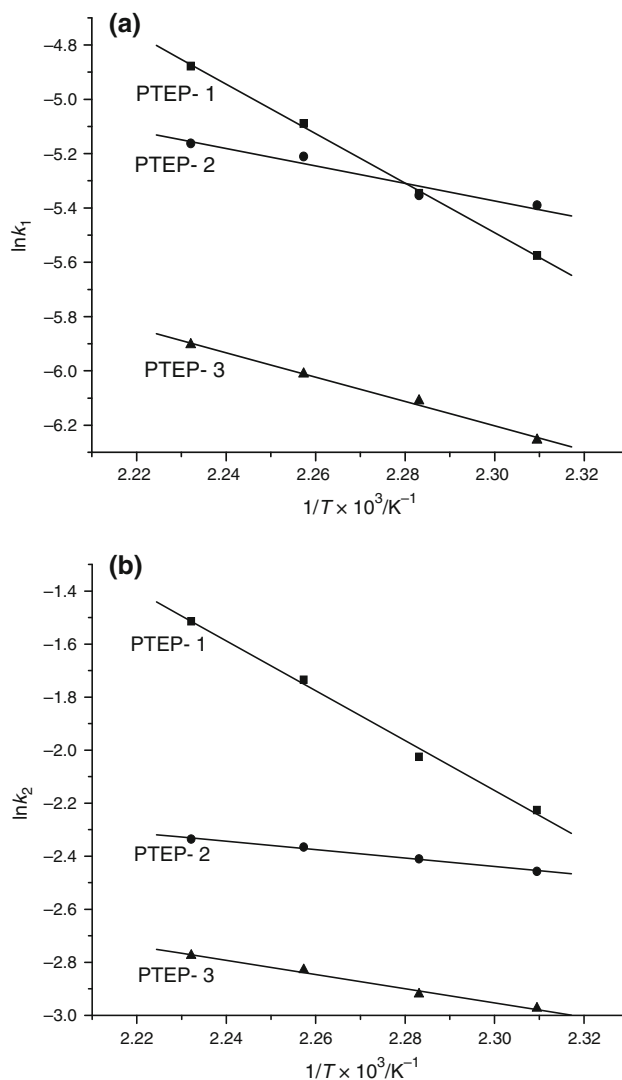
**Fig. 8** Multiple regression curve-fitting for different composition at 160 °C

Probable mechanism of catalysis and autocatalysis of epoxy–anhydride reaction

The accepted mechanism for epoxy–anhydride reaction is the triggering of the attack of anhydride by the residual hydroxyl groups present in the epoxy resin [17, 18]. These OH groups can also be generated by way of carboxy-epoxy reaction; COOH groups from PTAC could be involved on this one. The OH–anhydride reaction leads to a hemiester with the generation of COOH groups. The COOH groups thus generated and those present in PTAC could further catalyse the epoxy–anhydride reaction by way of hydrogen bonding with epoxy or anhydride groups or both (Scheme 3). This accounts for autocatalysis the reaction between epoxy groups and anhydride is promoted by COOH groups by hydrogen bonding that renders the C–O bond polarized and labile for nucleophilic attack. Hydrogen

**Table 2** Rheokinetic parameters of various compositions of DGEBA/PTAC/PMDA at different temperatures

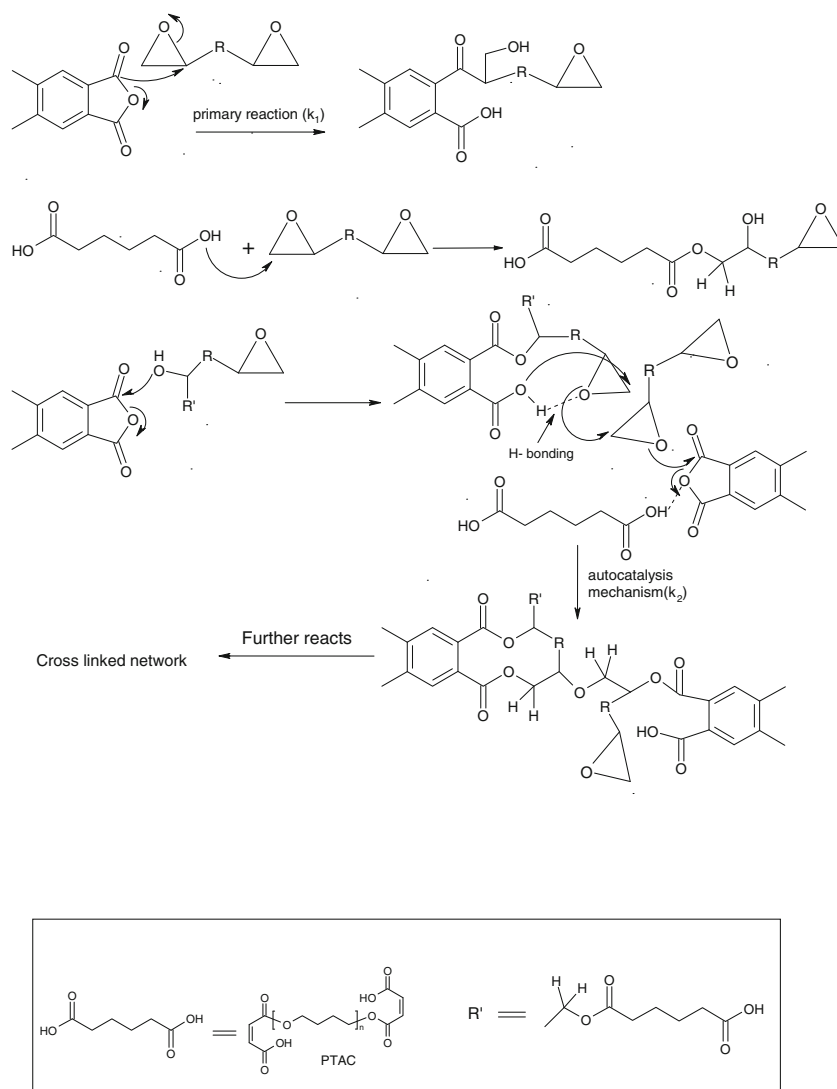
Composition	Temperature/ °C	$k_1 \times 10^{-3}/ \text{min}^{-1}$	$k_2 \times 10^{-1}/ \text{min}^{-1}$	$m$	$n$
PTEP-1	160	3.79	1.08	0.72	1.08
	165	4.77	1.32	0.93	1.06
	170	6.16	1.77	0.94	1.21
	175	7.61	2.20	1.22	1.72
PTEP-2	160	4.56	0.86	0.58	0.76
	165	4.73	0.90	0.88	1.29
	170	5.46	0.94	0.92	1.53
PTEP-3	160	1.92	0.51	0.74	0.75
	165	2.22	0.54	0.85	0.85
	170	2.45	0.59	0.82	1.17
	175	2.73	0.62	1.05	1.17



**Fig. 9** a Temperature dependence of  $k_1$  and b  $k_2$  of various compositions

**Table 3** Arrhenius parameters and reaction orders for different compositions

Composition	$m + n$	$E_1/\text{kJ mol}^{-1}$	$E_2/\text{kJ mol}^{-1}$	$A_1/\text{min}^{-1}$	$A_2/\text{min}^{-1}$
PTEP-1	2.22	75.6	77.9	$2.65 \times 10^8$	$5.03 \times 10^6$
PTEP-2	2.11	37.3	38.0	$2.93 \times 10^5$	$3.09 \times 10^4$
PTEP-3	2.00	26.2	28.2	$9.29 \times 10^4$	$2.44 \times 10^3$

**Scheme 3** Likely mechanism of COOH catalysis in the alcohol triggered epoxy–anhydride reaction, regenerating COOH group causing autocatalysis

bonding causes only a polarization of C–O bond, orienting the direction of attack on the oxirane. The network could also be formed by way of bond formation between oxygen atoms of one oxirane with carbon atom of another oxirane. All these possibilities are together depicted in Scheme 3.

#### Generalization of cure kinetic model

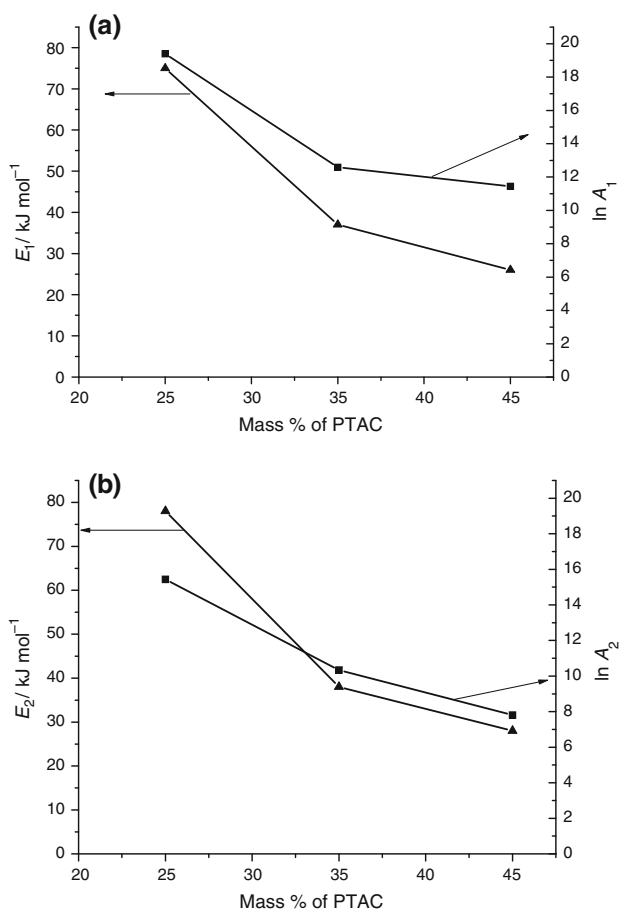
By substituting the kinetic parameters in Eq. 3, a generalized expression for overall rate of reaction could be arrived

at as in Eq. 5. The Eq. 5 is useful for predicting the isothermal reaction fractional conversion profile at a given temperature for a given composition. These predictions are made with a computer-aided numerical integration of the differential Eq. 5 that give ‘ $\alpha$ ’ at any time ‘ $t$ ’.

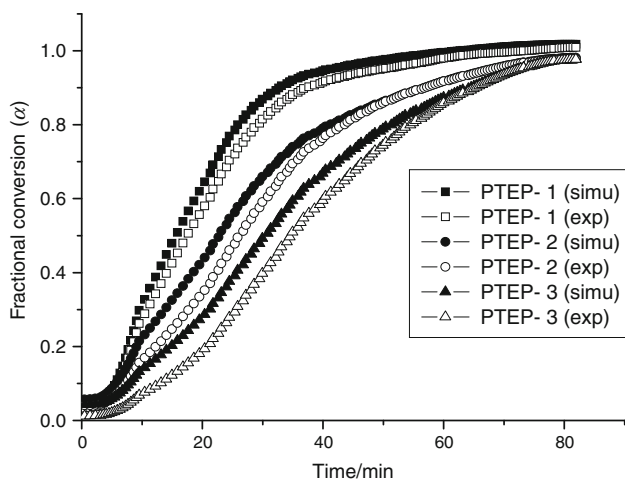
$$d\alpha/dt = A_1 e^{-E_1/RT} (1 - \alpha)^n + A_2 e^{-E_2/RT} \alpha^m (1 - \alpha)^n \quad (5)$$

Typical comparisons between the experimental and predicted fractional conversion profiles are shown in Fig. 11. The predicted profiles are in agreement with the





**Fig. 10** Variation of activation energies ( $E_1$  and  $E_2$ ) and frequency factor ( $A_1$  and  $A_2$ ) with PTAC concentration



**Fig. 11** Comparison of experimental and predicted isothermal reaction profiles of different compositions at 165 °C

experimental data for all the compositions. The knowledge about the parameters in Eq. 5 (i.e.  $A_1$ ,  $A_2$ ,  $E_1$  and  $E_2$ ) generated by the kinetic studies helped in generating the

time–conversion profile at any temperature. This helped predict the cure condition required for a composition at any given temperature without experimentation.

### Conclusions

The kinetics of the curing reaction of an epoxy resin cured by PMDA in presence of a co-curable and catalyst viz: carboxy telechelic PTMO conformed to an overall second-order, self-accelerated phenomenological model. The overall reaction order is independent of the compositions. The carboxylic acid group generated from PMDA by reaction of alcohol containing epoxy is probably responsible for the autocatalytic effect by way of hydrogen bonding of this group with oxirane and anhydride groups. The study revealed that though the activation energy decreased by the catalysis of COOH groups of PTAC, replacement of part PMDA by PTAC caused an overall decrease in rate of reaction. The autocatalysis needed more activation energy as it is caused by the COOH groups generated on the network and is located in a sterically hindered environment. The kinetic study helped in generating a master equation capable of predicting the cure profile of a given composition at a specified temperature. This helps in defining the cure time and temperature for any given composition to achieve a desired level of crosslinking. The shape memory properties of the cured polymers and composites will be presented in an ensuing publication.

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