



## Cure kinetics and thermodynamics of polyurethane network formation based on castor oil based polyester polyol and 4,4'-diphenyl methane diisocyanate

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In this work, isothermal curing kinetics of a non-catalysed and non-blown reaction between castor oil based polyester polyol and polymeric 4, 4'-diphenyl methane diisocyanate (MDI) has been investigated using Differential Scanning calorimeter (DSC) and viscosity build up studies. Several phenomenological models like Ozawa, Kissinger and Kissinger-Akahira-Sunose (KAS) isoconversional methods has been adopted to study polymerisation kinetics through DSC. DSC cure kinetics is studied at different heating rates (5°C/min, 10°C/min, 15°C/min and 20°C/min). Viscosity build up studies are also done for evaluating the kinetic parameters. These studies have been conducted for an isocyanate index [NCO equivalents/OH equivalents] of 1:1 and 1:2. Dynamic viscosity is measured as a function of time and rate constant and activation energy of the curing system is evaluated. Activation energy obtained for 1:1 index through Ozawa and Kissinger methods is found to be in the range of 70kJ/mol and for 1:2 index it is found to be in the range of 50kJ/mol. Thermodynamic parameters like Gibb's free energy (Activation Free Energy), activation enthalpy and activation entropy of the polymerisation kinetics is calculated using Wynne-Jones-Eyring-Evans Theory.

**Keywords:** Activation Energy, DSC, Polyurethane, Viscosity build up

Polyurethanes are a broad family of polymers with wide range of applications such as foams, adhesives sealants, coatings and simulators<sup>1</sup>. One of the prominent applications of polyurethane is thermal insulation material for storing cryogenic propellants. Traditional polyurethanes are produced by reacting polyol and polymeric 4,4' diphenyl methane diisocyanate (MDI)<sup>2</sup>. The polyurethane have received great attention as they possess a broad range of chemical and physical properties, good biocompatibility and can be designed to degrade biologically by varying their chemical compositions<sup>3</sup>. Knowledge of kinetic parameters of a reactive polymer resin is very important in the design and processing of polymer technologies.

For simple compounds, reaction kinetics can be evaluated through conventional quantitative functional group estimation techniques. In case of polymer curing, as the polymer becomes insoluble beyond gel point, traditional titrimetric methods are of little use<sup>4</sup>. In such cases, dynamic DSC will be a very useful tool. Simultaneously, spindle type viscometer allows the determination of viscosities of the crosslinking polymer only below the gel point.

Manu et al studied the kinetics of glycidyl azide polymer based urethane network formation by Fourier transform infrared spectroscopy and viscosity build up studies. They evaluated rate constant and activation energy of the curing system. Thermodynamics of the system was investigated by Eyring theory.<sup>4</sup>

Yiyi Xiao *et al.* investigated the isothermal curing kinetics of hydroxyl-terminated polybutadiene (HTPB) binder system containing dioctylsebacate (DOS) and polyaryl polyisocyanate (PAPI) through microcalorimetry. They found out that as the temperature increases the curing was completed at shorter period of time. Activation enthalpy, activation entropy and Gibb's free energy for the curing system was also evaluated<sup>5</sup>.

Tejado *et al.* analysed cure kinetics of two lignin based novolac type phenolic resin systems with commercial novolac system by applying simple and isoconversional kinetic models to empirical data obtained by DSC. Several models like Ozawa, Kissinger and KAS methods had been utilised to compare the cure kinetics<sup>6</sup>.

He Sun *et al.* designed a new thermal curing system with two-stage curing characteristics. The two-stage curing system contain matrix epoxy resin E51, room temperature curing agent 593 and latent curing agent 594, and these two curing agents have rarely reciprocity between each other. The reaction behaviours of two different curing processes have been systematically studied. The non-isothermal differential scanning calorimetry (DSC) test was used to discuss the curing reaction of two stages curing, and the data obtained from the curves were used to calculate the kinetic parameters. Kissinger-Akahira-Sunose (KAS) method was applied to determine activation energy ( $E_a$ ) and investigate it as the change of conversion<sup>7</sup>.

Sekkar *et al.* conducted rheokinetic studies on bulk polymerization reaction between hydroxyl terminated polybutadiene (HTPB) and di-isocyanates such as toluene-di-isocyanate (TDI), hexamethylene-di-isocyanate (HMDI), and isophorone-di-isocyanate (IPDI) by following the build-up of viscosity of the reaction mixture during the cure reaction. Rheo-kinetic plots were obtained by plotting  $\ln$  (viscosity) vs. time<sup>8</sup>.

Jain *et al.* had undertaken the cure kinetics for the formation of copolyurethane networks of various compositions based on hydroxyl-terminated polybutadiene (HTPB), poly (12-hydroxy stearic acid-co-TMP) ester polyol (PEP), and different isocyanate through viscosity build up during the cure reaction<sup>9</sup>.

The main aim of this work is to explore the curing kinetics of polyurethane network formation from castor oil based polyester polyol and MDI. Polymerisation kinetic parameters were evaluated using several methods like Ozawa, Kissinger and KAS isoconversional methods and were compared. Rheokinetic studies of the polyurethane network formation were undertaken through build-up of viscosity during cure reaction. Kinetic parameters were evaluated by plotting viscosity versus time graph. Thermodynamic parameters like Gibbs free energy, activation energy and entropy of the polyurethane network formation were considered using Eyring Equation.

## Kinetic Modelling

### Non Isothermal methods

Polyurethane curing process is second order reaction kinetics<sup>13</sup>. DSC technique is a very powerful tool to evaluate the curing kinetics of thermosetting

resins as it allows the calculation of kinetic parameter from thermograms by relating the heat flow to the reaction rate<sup>6</sup>. All phenomenological models are derived from equation 1 which relates reaction rate to a conversion function through a reaction constant, which is temperature dependent.

$$\frac{d\alpha}{dt} = A \exp\left[\frac{-E_a}{RT}\right] f(\alpha) \quad \dots (1)$$

Where  $d\alpha/dt$  is the rate of reaction,  $E_a$  is the activation energy,  $R$  is universal gas constant ( $R=8.314$  J/ K mol),  $T$  is the temperature,  $f(\alpha)$  is the conversion function,  $A$  is the Arrhenius frequency factor.

In case of non isothermal methods when temperature is raised at a constant heating rate ( $\beta$ ) integral form of the kinetic equation can be expressed as;<sup>[3]</sup>.

$$g(\alpha) = \frac{A}{\beta} \int_0^{\alpha} \exp\left[\frac{-E_a}{RT}\right] dT \quad \dots (2)$$

The use of different approximations to solve the temperature integral give rise to Ozawa and Kissinger equation where the activation energy is related to heating rate and temperature at the peak of the exothermic curve ( $T_p$ ) obtained by DSC.

Equation 3 gives the expression for Ozawa method and equation 4 explains Kissinger method.

$$-\ln(\beta) = 1.0516 \left(\frac{E_a}{RT_p}\right) - A' \quad \dots (3)$$

$$-\ln\left(\frac{\beta}{T_p^2}\right) = \frac{E_a}{RT_p} - \ln\left(\frac{A'R}{E_a}\right) \quad \dots (4)$$

From the above equations, a plot of  $-\ln(\beta)$  vs.  $1/T_p$  or a plot of  $-\ln(\beta/T_p^2)$  vs.  $1/T_p$  gives straight line from which activation energy can be found out.

### Isoconversional Method

Isoconversional models are based on the assumption that for a given conversion grade activation energy remains constant regardless of the curing temperature. [6]. KAS model was used to determine the kinetic parameters of polyurethane cure reaction.

Conversion grade is given as

$$\alpha = \frac{\Delta H_\alpha}{\Delta H_0} \quad \dots (5)$$

Where  $\Delta H_\alpha$  is the heat released at a given conversion value and  $\Delta H_0$  is the total heat released during the end of the reaction.

From the above expression which relates the conversion with enthalpy, following expression is obtained for KAS model.

$$-\ln\left(\frac{\beta}{T_p^2}\right) = \frac{E_\alpha}{RT_\alpha} - \ln\left(\frac{A'_\alpha R}{E_\alpha}\right) \quad \dots (6)$$

$E_\alpha$  is the activation energy associated with each conversion grade,  $T_\alpha$  is the single temperature for each conversion grade. Thus by plotting  $-\ln\left(\frac{\beta}{T_p^2}\right)$  vs.

$1/T_\alpha$  a straight line is obtained and from the slope  $\frac{E_\alpha}{RT_\alpha}$  can be determined.

#### Rheo kinetic modelling: Determination of rate constants through viscosity builds up studies

Viscosity of the curing mixture increases with time as polyurethane network formation advances. The viscosity build up during the cure process is mainly due to two factors: (i) increase in molecular weight as a result of polymer chain growth; (ii) chain branching due to the presence of tri- or higher functional moieties present in the prepolymer or in the additives. Viscosity ( $\eta_t$ ) of the curing system (leading to polyurethane network formation) at any given time  $t$ , could be related to time in the form of an exponential function as given below<sup>4</sup>.

$$\eta_t = \eta_0 e^{k_v t} \quad \dots (7)$$

Where  $\eta_0$  is the viscosity at  $t=0$ ,  $k_v$  is the rate constant for viscosity build up and  $t$  is the time. By plotting  $\ln \eta_t$  vs. time a straight line is obtained from which rate constant can be evaluated.

Activation energy of the curing reaction can be evaluated by Arrhenius equation which  $c$  is given below<sup>4</sup>.

$$k = k_0 e^{\frac{-E_a}{RT}} \quad \dots (8)$$

where  $k$  is the rate constant and  $k_0$  is the pre exponential factor. By plotting  $\ln k$  vs.  $1/T$  provides a straight line and from the slope  $-E_a/R$ , activation energy can be found out.

#### Thermodynamics

For evaluating thermodynamic parameters like activation enthalpy, Wynnes-Jones-Eyring-Evans theory gives the following expression. [4].

$$\ln\left(\frac{k}{T}\right) = \frac{-\Delta H^E}{RT} + \ln\left(\frac{k_N}{h}\right) + \frac{\Delta S^E}{R} \quad \dots (9)$$

Where  $\Delta H^E$  is the activation enthalpy,  $\Delta S^E$  is the activation entropy,  $k_N$  is Boltzmann constant ( $1.3807 \times 10^{-23} \text{ JK}^{-1}$ ),  $h$  is Planck's constant ( $6.626 \times 10^{-34} \text{ Js}^{-1}$ ).

For evaluating Gibb's free energy (activation free energy) following expression can be used; [5, 11].

$$\Delta G^E = -RT \ln \frac{RT}{Nhk} \quad \dots (10)$$

where  $N$  is the Avogadro's number ( $6.024 \times 10^{23} \text{ mol}^{-1}$ ). From 11 and 12, activation enthalpy, activation entropy and Activation free energy can be calculated at different temperatures.

#### Experimental Section

##### Materials

Polyester polyol with hydroxyl value of 452 mg KOH/g synthesised indigenously by modifying castor oil through polyesterification reaction was used for the present study. MDI with isocyanate content 29-33%, obtained from M/s Surabhi Industries Pune, was used as the curing agent.

##### Preparation of polyurethane

For DSC analysis polyester polyol and MDI were reacted together at an isocyanate index of 1:1 and 1:2. For viscosity build up studies isocyanate index used was 1:1. Isocyanate index was calculated as

$$\text{Isocyanate Index} = \frac{NCO \text{ equivalent}}{OH \text{ equivalent}} \quad \dots (11)$$

##### DSC measurements

Non isothermal curing studies were carried out in TA Instruments DSC Q-20 Differential Scanning Calorimeter. Approximately 5 mg samples were taken in aluminium crucibles and experiments were conducted under nitrogen atmosphere (50 mL/min) at four different heating rates viz, 5°C/min, 10°C/min, 15°C/min and 20°C/min.

##### Viscosity measurements

A RVDV II model Brookfield viscometer was used to measure the viscosity during the curing reaction. The sample cell used was small sample adaptor of

10 mL capacity and the spindle used was S-21. Viscosity of the curing mixture was recorded at various intervals of time. Viscosity build up studies were conducted at different temperatures.

## Results and Discussion

### DSC experiments

Non -Isothermal scans were run at temperatures typically around 20°C to 200°C at heating rates of 5°C/min, 10°C/min, 15°C/min and 20°C/min. Cure kinetics of polyurethane formation was studied for an isocyanate index of 1:1 and 1:2. Figure 1 shows thermograms obtained by DSC for polyurethane network formation for 1:1 and 1:2 index runs at the above heating rates. Peak temperature  $T_p$  obtained are reported in Table 1. These data were used to evaluate the kinetic parameters through Ozawa and Kissinger Methods and for KAS isoconversional method. Because of the high reactivity, the reaction will start

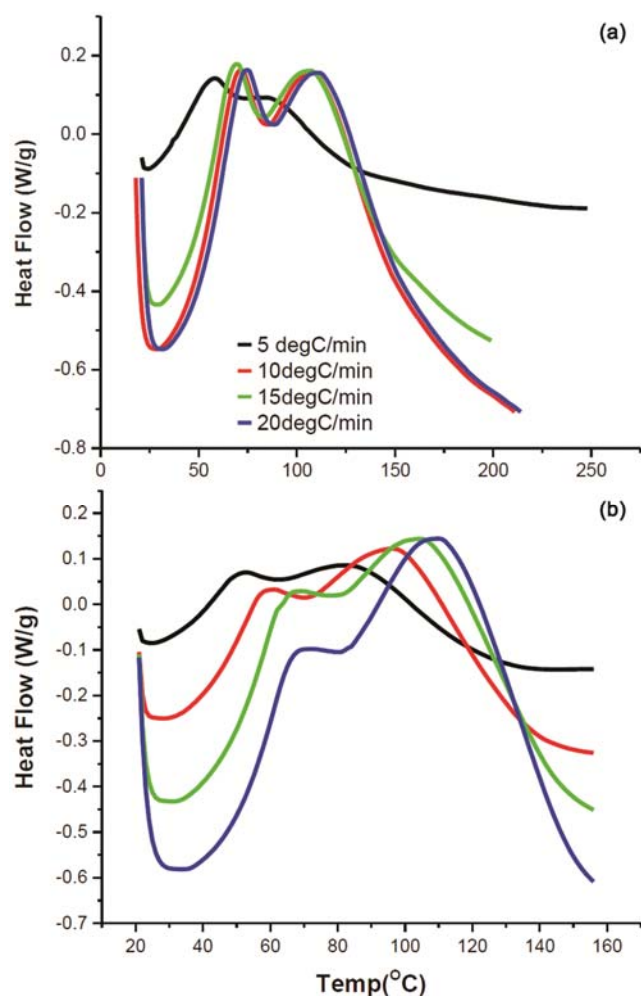


Fig. 1 — DSC plots for (a) 1:1 (b) 1:2 isocyanate index

as soon as the isocyanate and polyol are mixed. The sample preparation was done swiftly in order to avoid loss of data during the first stages of the reaction. The relative area under the curves up to a given temperature is a good measure of the conversion. In all curves a shoulder on the right side can be distinguished. This is due to the fact that polyester polyol contains both primary and secondary hydroxyl groups in which reactivity of secondary hydroxyl group is less compared to primary.

### Ozawa and Kissinger methods

Figures 2 and 3 describe Ozawa and Kissinger Plots according to equation 3 and 4 for 1:1 and 1:2 isocyanate index. Kinetic parameters obtained are reported in Table 2. As can be seen in Table 2, in both the cases, polyurethane curing process proceeds much faster for an isocyanate index of 1:2 compared to 1:1.

### KAS Isoconversional Method

Figures 4 and 5 shows the conversion,  $\alpha$  vs. Temp curves at different heating rates for 1:1 and 1:2 isocyanate index. Figure 6 shows the plot according to equation 8, which yields a straight line

Table 1 — Temperature at the peak exothermic curve ( $T_p$ ) for different heating rates and Isocyanate Index

Heating rates, $\beta$ °C/min	$T_p$ °C	
	Isocyanate Index	Isocyanate Index
	1:1	1:2
5	58	82
10	66	95
15	70	104
20	75	110

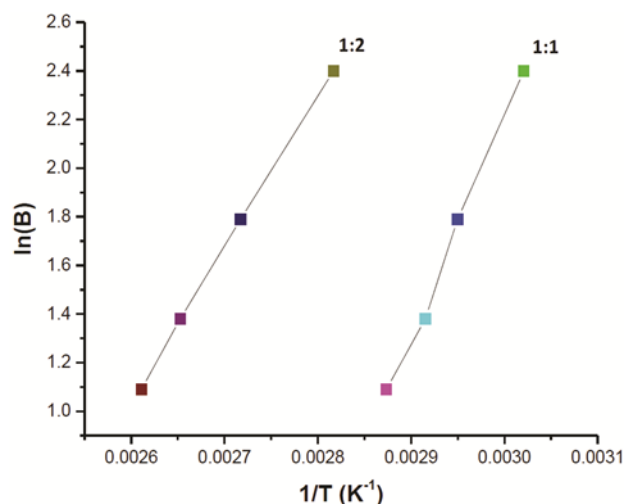


Fig. 2 — Ozawa Model for 1:1 and 1:2 isocyanate index

with slope,  $E\alpha/R$ , from which global activation energy for the curing process can be found out. Figure 7 gives the activation energy for each conversion based on KAS model. From this figure it is clear that activation energy is almost constant throughout the process which indicates that cure reaction is dominated by a single reaction type namely addition reaction<sup>6</sup>.

Table 2 — Activation energy obtained by different methods

Methods	Isocyanate Index	Activation energy kJ/mol	Correlation coefficient ( $R^2$ )
Ozawa	1:1	75.38	0.9939
	1:2	52.61	0.9994
Kissinger	1:1	74.38	0.9935
	1:2	49.57	0.9994

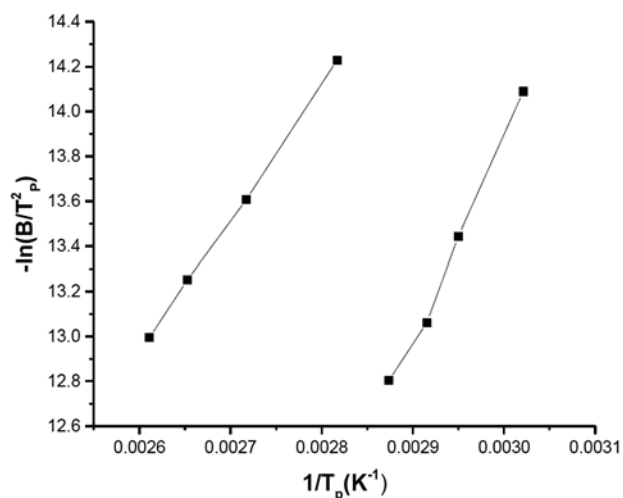


Fig. 3 — Kissinger Method for 1:1 and 1:2 isocyanate Index

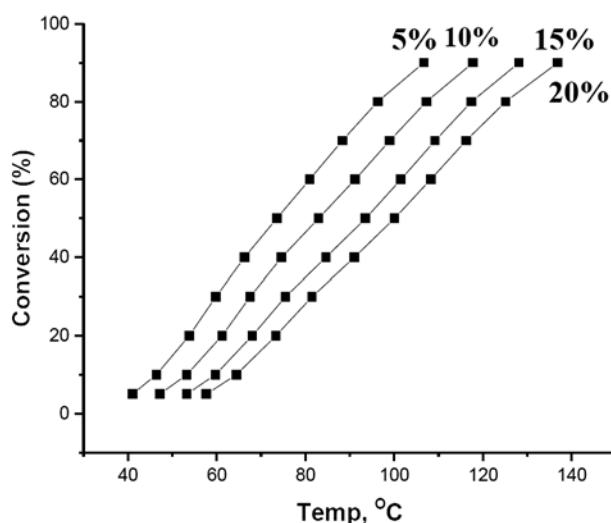


Fig. 4 — Conversion for 1:1 isocyanate index at different heating rates

#### Viscosity build up

Figure 8 shows isothermal rheometer data at different temperatures. During initial stage, a small viscosity build up was observed, and after a particular time the viscosity suddenly increases sharply. This

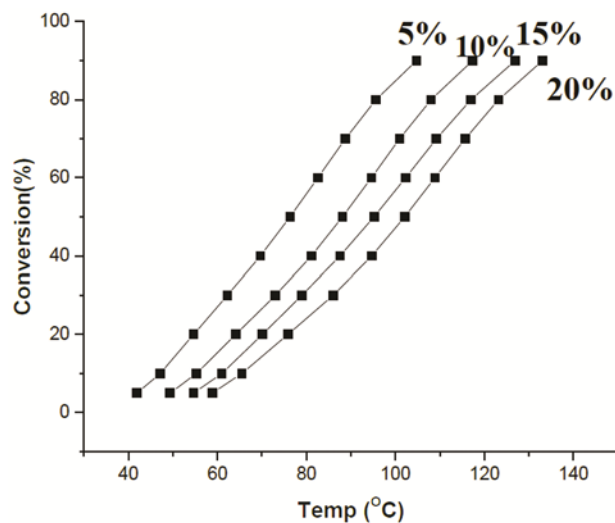


Fig. 5 — Conversion for 1:2 isocyanate index at different heating rates

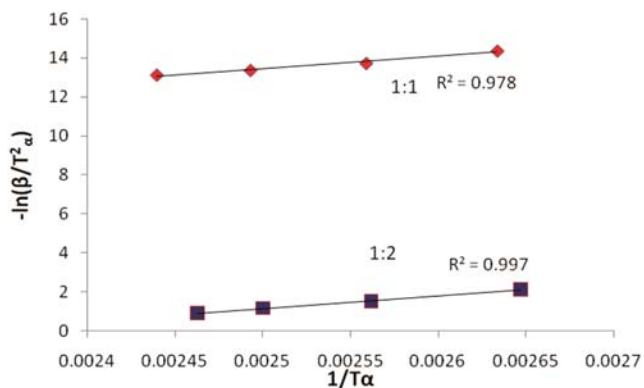


Fig. 6 — KAS model for 90% conversion for 1:1 and 1:2 isocyanate Index

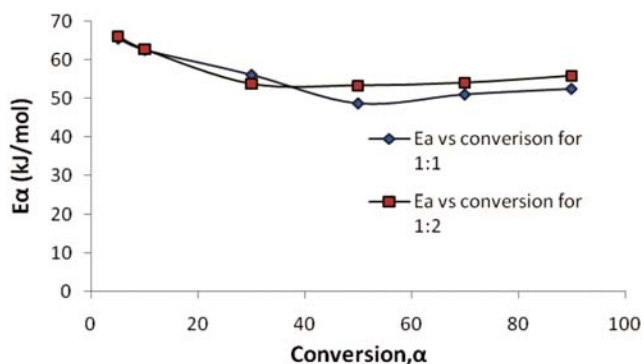


Fig. 7 — Activation energy with conversion based on isoconversional method

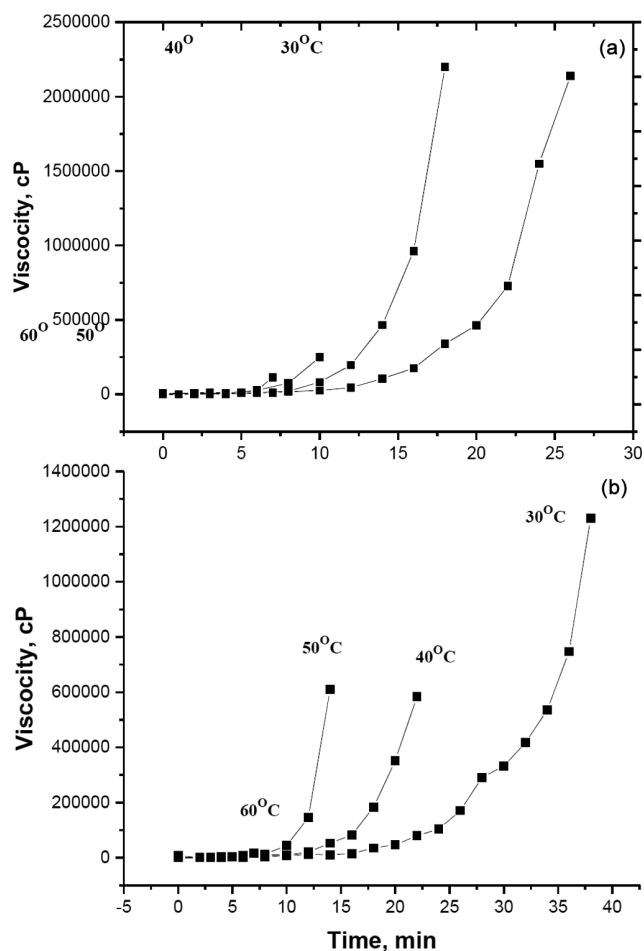


Fig. 8 — Viscosity build up during curing of polyurethane at different temperatures (a): 1:1 isocyanate Index (b): 1:2 isocyanate index

process is called gelation which involves the formation of an infinite network due to which the viscosity increases to infinity. From a liquid-like behaviour the system turns into solid-like behaviour<sup>10</sup>.

Figure 9 shows the plot of  $\ln$  viscosity vs Time at different temperatures. As per equation 7 by plotting  $\ln k$  vs Time, rate constants at different temperatures can be evaluated.

Activation energy for the curing process can be evaluated by plotting  $\ln k$  vs  $1/T$ . From the slope of this plot, activation energy can be estimated (Table 3).

#### Thermodynamics

Eyring plot is plotted from which thermodynamic parameters like activation enthalpy and activation entropy were determined. Values of thermodynamic parameters are listed in Table 4. Overall, negative entropy at the transition state of the reaction was found, indicating that species in these transition states

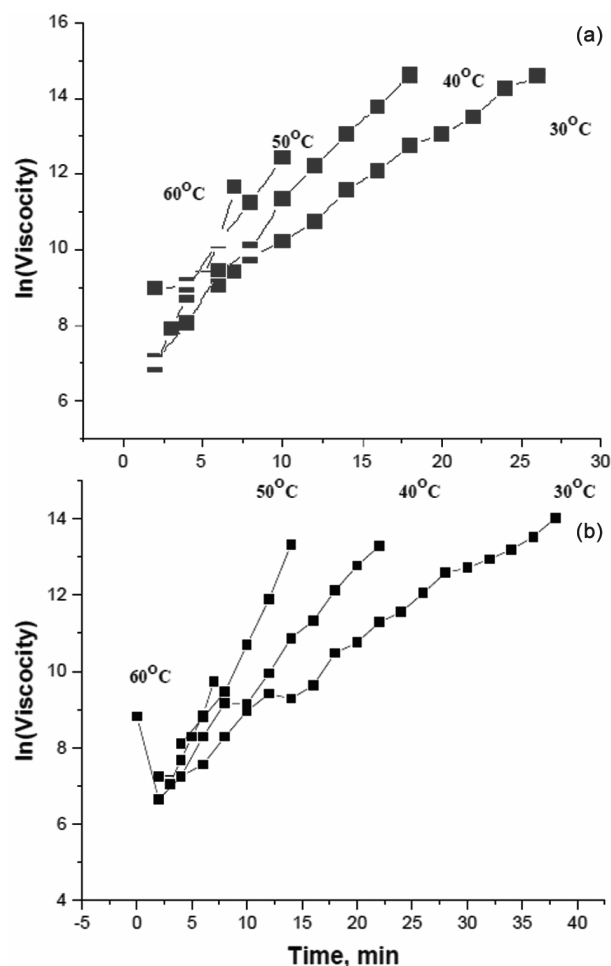


Fig. 9 — Plot of  $\ln$  (Viscosity) vs Time at different temperatures (a): 1:1 Isocyanate Index (b): 1:2 isocyanate Index

Table 3 — Kinetic parameters from viscosity build up studies

Temperature, °C	Rate constant mol/min		Activation energy, kJ/mol	
	1:1	1:2	1:1	1:2
30	0.25	0.19	29.74	37.31
40	0.45	0.28		
50	0.53	0.53		
60	0.76	0.67		

Table 4 — Thermodynamic parameters for polyurethane curing

Isocyanate Index	$\Delta H^\ddagger$ (kJ/mol)	$\Delta S^\ddagger$ (J/mol K)
1:1	27.105	-166.51
1:2	34.67	-144.58

have fewer degrees of freedom or less molecular mobility<sup>12</sup>. Activation free energy or Gibbs free energy for the polyurethane curing process are listed in Table 5. Negative Activation free energy suggests that the reaction is exothermic in nature and also spontaneous.

Table 5 — Activation Free energy at various temperatures

Temp K	$\Delta G^\ddagger$ kJ/mol	
	1:1	1:2
303	-77.59	-78.43
313	-78.84	-80.09
323	-81.01	-81.02
333	-82.61	-82.97

### Conclusion

The non- isothermal curing kinetics of polyester polyol-isocyanate was investigated using DSC. Data obtained from DSC was used to evaluate the kinetic parameters using various methods like Ozawa, Kissinger and KAS isoconversional methods. From Ozawa and Kissinger method it is very clear that for an isocyanate index of 1: 2 activation energy required was less compared to that for an index of 1:1. Isoconversional method suggests that the curing reaction of polyol-isocyanate was predominant with single reaction type. These methods can be correlated with viscosity build up data. Rate constant (k) at different temperatures were evaluated through viscosity build up studies. From the kinetic parameters, thermodynamics of polyurethane curing process such as total entropy and Gibb's free energy of the system was studied. Gibb's free energy was found to be negative which suggests that transition state during curing process was in orderly state compared to that of ground state and curing process is exothermic and spontaneous.

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