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Dedicated to Prof. Edith A. Turi in recognition of her leadership in education

A DSC STUDY ON CURE KINETICS OF HTPB-IPDI URETHANE REACTION

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Abstract

The kinetics of the urethane-forming cure reaction of hydroxyl terminated polybutadiene (HTPB) with isophorone diisocyanate (IPDI) in presence of ferric tris (acetyl acetonate) (FeAA) catalyst was investigated using differential scanning calorimetry (DSC). The Arrhenius activation parameters, viz., activation energy E and pre-exponential factor A were evaluated using the non-isothermal integral Coats-Redfern equation. The cure reaction was catalysed by ferric acetyl acetonate (FeAA), as revealed from the decrease in reaction temperatures and the increase in rate constants; however, the computed activation energy did not show any correlation to the catalyst concentration. The values of E and A for the uncatalysed reaction at different heating rates showed interdependence through kinetic compensation (*KC*) effect. Using *KC* correction, E values were normalised for the value of A for the uncatalysed reaction under identical conditions. The normalised E values decreased exponentially with increase in concentration of FeAA, showing high propensity of the HTPB-IPDI system for catalysis.

Keywords: catalyst, cure kinetics, DSC, HTPB, kinetic compensation effect, urethane

Introduction

Hydroxyl terminated polybutadiene (HTPB) liquid prepolymers find extensive application as binders in composite solid propellants for launch vehicle technology [1]. The composite solid propellant comprises of 12–20% of polymeric fuel binder, a metal additive such as aluminium powder and an oxidiser, usually ammonium perchlorate. The binder in the solid propellant imparts dimensional stability and structural integrity to the grain and also acts as fuel during combustion. HTPB polymers are generally prepared by hydrogen peroxide initiated free radical polymerisation of 1,4-butadiene [2] and are functional telechelic polymers containing mostly terminal hydroxyl groups. The hydroxyl functional groups of HTPB undergo stoichiometric urethane reaction with a variety of isocyanates to form the polyurethane network resulting in propellants with good mechanical properties. The mechanical properties of the propellant is largely determined by the extent of polyurethane formation [3, 4]. Hence a knowledge of the kinetics of polyurethane formation will be very useful in

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the design of propellants, liners, etc., possessing mechanical properties needed for specific purposes.

Conventionally toluene diisocyanate (TDI) is used as a curative for HTPB to form crosslinked urethane networks. Urethane formation is a fairly rapid reaction with TDI. Since this limits the useful pot life of the propellant, lesser reactive isophorone diisocyante (IPDI) [5] is more suitable in propellant formulations where a high pot life of the propellant paste is needed for processing big size grains. Cure catalysts are sometimes added in small quantities to control the rate of cure or to minimise the side reactions occurring during the course of curing. In the absence of a catalyst, the cure reaction may be very slow or incomplete.

The cure reaction of HTPB with various curatives has been investigated by several workers using various techniques, with relatively more literature available on solution kinetics of the urethane formation [6–12]. Thermoanalytical techniques, especially DSC is extensively employed to study the cure reactions in polymers [13–20]. Both isothermal and dynamic methods are used although dynamic DSC is more beneficial in cases where the enthalpy change is relatively less. A knowledge of the enthalpy changes and the kinetics of cure reaction is of utmost importance for better understanding of the process of curing. The main objective of the present study is to utilise the dynamic DSC data to establish (i) the kinetic parameters of the HTPB-IPDI urethane reaction using the non-isothermal integral approach, (ii) normalization of activation energy through the kinetic compensation correction and (iii) the effect of catalyst concentration on the activation energy of the cure reaction. The isocyanate chosen in our study was IPDI and the catalyst was ferric tris (acetyl acetonate).

Experimental

Materials and methods

HTPB resin used was manufactured at Vikram Sarabhai Space Centre, India by the free-radical polymerisation of butadiene using hydrogen peroxide as initiator and has the following important characteristics : hydroxyl value=42 mg KOH/g, number average molecular weight =2690, viscosity at 30°C=5800 cps and polydispersity =2.4. The resin is predominantly bifunctional but also contains some extent of tri- and polyfunctional moities so that it gets cured by a diisocyanate [21]. IPDI curator obtained from Fluka AG was used for the curing studies. FeAA (Merck) was used as received.

Instrumental

Curing studies were conducted on a TA Instruments MDSC 2920 in standard DSC mode under ultra-pure argon (99.99%) atmosphere at a flow rate of 50 mL min^{-1}. A sample mass of 20±0.5 mg was used in all cases. For all the cure studies, the DSC cell was cooled to an initial temperature of 10°C using a TA Instruments Refrigerated Cooling System (RCS). The DSC instrument was calibrated for temperature and heat flow using indium metal standard (MP=156.6°C, ΔH=28.45 J g^{-1}). The duplicate DSC experiments performed gave DSC peak temperature in the range of ±2°C, kinetic parameters within 5% and enthalpy change within 5%, and the mean values are reported in these cases. FTIR spectra were recorded on a Nicolet 510P spectrometer using NaCl cell. Data analysis was done on an IBM Personal Computer using Origin software.

Curing Studies

HTPB and IPDI were mixed in 1:1 equivalent ratio and the cure reaction was studied at various heating rates from 4°C to 15°C min^{-1} using DSC. Samples were taken in aluminium hermetic pans. The effect of catalyst on the cure reaction was studied at eight different catalyst concentrations in the range of 0.02 to 0.5 wt% of FeAA at a constant heating rate of 5°C min^{-1}.

Results and discussion

Heat of cure

The DSC exothermic curves were used to evaluate the heat of cure (ΔH) and kinetic parameters of the cure reaction. The heat of cure is directly proportional to the area under the DSC curve and is calculated by area integration software. The fractional conversion, α, calculated from the fractional and total areas under the DSC curve was used for the computation of the kinetic parameters.

Table 1 DSC data of uncatalysed and catalysed HTPB-IPDI reaction

No.	Catalyst conc./%	T_i/°C	T_s/°C	T_f/°C	ΔH/J g^{-1}
1	0.00	60	130	212	18
2	0.02	38	91	160	38
3	0.05	25	61	127	32
4	0.08	23	65	131	27
5	0.10	22	56	135	34
6	0.20	21	59	136	34
7	0.30	20	54	126	28
8	0.40	21	53	123	27
9	0.50	20	51	124	25

The effect of catalyst concentrations in the range of 0.02 to 0.5 weight% of the resin system on the DSC cure reaction was studied at a heating rate of 5°C min^{-1} and the results are given in Table 1. All the reactions studied showed smooth exothermic curves. The temperature of initiation of reaction T_i, peak exothermic temperature T_s and the temperature of completion of reaction T_f are given in Table 1 which also gives the corresponding values for the cure reaction without any catalyst. From this Table, it can be seen that the reaction temperatures show a substantial decrease in the catalysed reactions. The efficacy of the catalyst is seen in Fig. 1 showing T_i, T_s and T_f

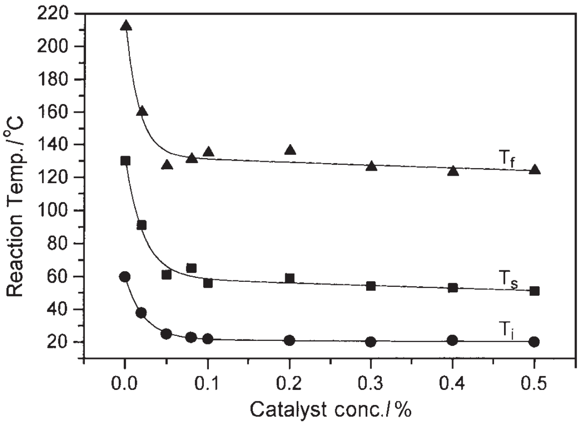

Fig. 1 Reaction temperatures (T_i, T_s and T_f) *vs.* catalyst concentration

vs. catalyst concentration. The exponential nature of reaction temperatures *vs.* catalyst concentration curves is a confirmation to the high propensity of the HTPB-IPDI cure reaction for catalysis. The catalyst is most effective upto a concentration range of around 0.05% and thereafter the effectiveness slowly tapers. The relation between the catalyst concentration (c) and the temperatures of the reaction (T) has been established from the best-fit curves as

$$T = a_1 + a_2\,\mathrm{e}^{-c/b1} + a_3\,\mathrm{e}^{-c/b2}$$

where a_1, a_2, a_3, b_1 and b_2 are empirical constants whose values are given in Table 2.

Table 2 Curve-fit constants for reaction temperature *vs.* catalyst concentration curves

Reaction temp./°C	a_1	a_2	a_3	b_1	b_2
T_i	19.70	38.20	21.97	0.0227	0.3424
T_s	38.25	71.12	21.22	0.0225	1.102
T_f	70.94	79.76	61.92	0.0166	3.187

The values of heat of cure reaction ΔH calculated from DSC experiments (Table 1) were randomly fluctuating from 28 to 35 J g^{-1} for the catalysed reaction, the reason for the fluctuation being the low magnitude of enthalpy accompanying the cure reaction spanning over 100°C. The ΔH values of the catalysed reaction is nearly twice that of the uncatalysed reaction. FTIR spectra of the samples recorded both at the time of mixing and immediately after completion of DSC cure showed the complete disappearance of the –NCO peak (2260 cm^{-1}) after cure for the catalysed reaction, whereas –NCO was present in the uncatalysed system though to a very small extent, indicating a minute residual cure which was confirmed by conducting repeat DSC analysis of all cured samples. No residual cure was observed in the catalysed system whereas very feeble exotherm was observed for the uncatalysed system. The small residual cure and the longer span of the reaction (152°C) probably result in lower magnitude of ΔH from the DSC experiments of the uncatalysed system.

Kinetics of cure

The kinetic parameters of the cure reactions of both catalysed and uncatalysed resin systems were evaluated using the Coats-Redfern equation [22]

$$\ln\{g(\alpha)/T^2\} = \ln\{(AR/\phi E)(1-2RT/E)\} - E/RT$$

where $g(\alpha)=[1-(1-\alpha)^{1-n}]/(1-n)$ for all values of n except n=1 for which $g(\alpha)= -\ln(1-\alpha)$, R is the universal gas constant, ϕ is the heating rate, E is the activation energy and A is the pre-exponential factor.

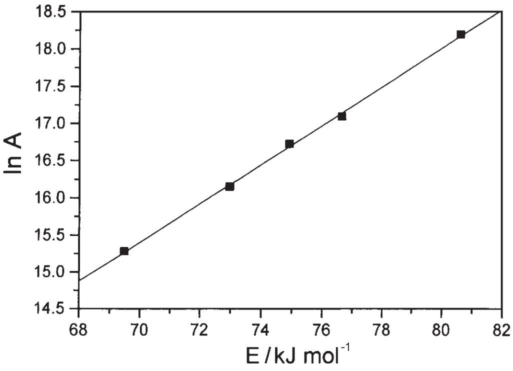

Fig. 2 Kinetic compensation plot

The order of the reaction was found to be 2 from the best fit linear plots of $\ln(g(\alpha)/T^2)$ *vs.* reciprocal of absolute temperature ($1/T$). A similar value (n=2) has been reported earlier for HTPB using other techniques [6, 23]. In majority of cases the best-fit value of n was 2. The values of E and A were determined from the Coats-Redfern linear plots using the predetermined optimum value of n and the results are given in Table 3. The correlation coefficient for all the Coats-Redfern kinetic plots were greater than 0.99, indicating the goodness of the curve fits. It is observed from Table 3 that both E and A values are different for all the nine cases studied. Since reaction rate depends on both E and A through the Arrhenius equation, $k=Ae^{-E/RT}$, the effect of the catalyst cannot be unequivocally assessed from the lowering of E values alone. We have, therefore, calculated the rate constants k at a fixed temperature of 60°C (T_i of the uncatalysed cure reaction) using the E and A values. The results are given in Table 3 from which it is seen that the rate constants are almost two orders of magnitude higher in the catalysed reactions, showing the efficacy of the catalyst, which was also clearly seen in the lowering of the reaction temperatures (Table 1 and Fig. 1). However, the activation energy values in Table 3 are higher for most of the catalysed reactions, contrary to the generally accepted trend of lowered activation energy for a reaction whose rate is enhanced by a catalyst. This discrepancy could be due to the fact that along with activation energy, the pre-exponential factor A also showed variations in these cases. If both E and A are altered in a reaction, a direct correlation of activation energy with the reaction rate becomes valid only after a normalisation for the corresponding change in A values expressed as 'kinetic compensation effect' showing a linear relationship between $\ln A$ and E as: $\ln A=a+bE$, where a and b are constants [24].

Table 3 Kinetic parameters of catalysed reactions

No.	Catalyst conc./%	E/kJ mol^{-1}	$\ln A$	Rate constant, k/s^{-1} at 60°C	E (for $\ln A$=16.15)
1	0.00	72.97	16.15	$3.74\cdot10^{-5}$	72.97
2	0.02	78.86	22.38	$2.23\cdot10^{-3}$	62.96
3	0.05	86.79	25.83	$4.03\cdot10^{-3}$	61.77
4	0.08	82.10	23.88	$3.11\cdot10^{-3}$	62.26
5	0.10	71.23	20.16	$3.80\cdot10^{-3}$	61.22
6	0.20	71.74	20.35	$3.84\cdot10^{-3}$	61.12
7	0.30	77.91	22.95	$5.57\cdot10^{-3}$	61.00
8	0.40	76.33	22.53	$6.51\cdot10^{-3}$	60.32
9	0.50	74.33	21.83	$6.62\cdot10^{-3}$	60.15

In order to establish the applicability of kinetic compensation effect in HTPB-IPDI reaction, the uncatalysed cure reaction was carried out at 5 different heating rates and the DSC data along with the results of the kinetic parameters computed using the Coats-Redfern equation are given in Table 4. It is observed that while T_i is nearly constant, T_s and T_f increase systematically with increase in heating rate. It is also noted that E and $\ln A$ show a similar increase, indicating kinetic compensation (*KC*) effect . The *KC* plot using the E and $\ln A$ values is shown in Fig. 2 and it follows the equation: $\ln A=-2.873+0.261E$, with correlation coefficient =0.9995. The good linearity of the *KC* curve confirms the prevalence of kinetic compensation for the HTPB-IPDI cure reaction, which implies that the change in activation energy with experimental conditions is only apparent in this case and its effect is compensated by a corresponding change in the value of $\ln A$. When a variation in activation energy is caused by the presence of a catalyst in such cases, it is necessary to apportion the effects due to kinetic compensation and the catalyst. For this purpose it is necessary to normalise the E values for a fixed value of A, and the most appropriate value of $\ln A$ in this case is that of the uncatalysed reaction. This was obtained as $\ln A$=16.15 for the uncatalysed reaction at 5°C min^{-1} heating rate. All catalysed reactions were conducted at this same heating rate.

The possibility of normalising activation energy for the data from a single non-isothermal experiment was recently examined in the case of the catalytic decomposition of ammonium perchlorate, and it was observed that the E values corrected in this manner showed good correlation to the effect of the catalyst, whereas no correla-

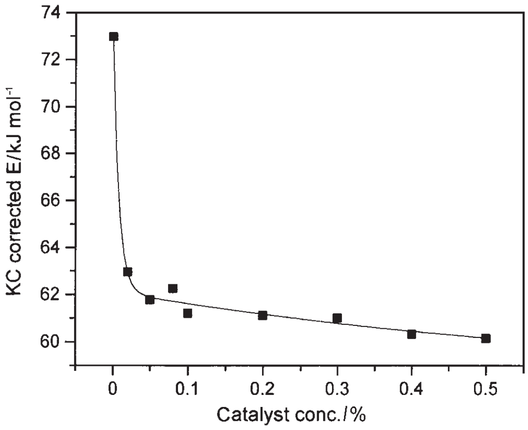

Fig. 3 *KC* corrected E values *vs*. catalyst concentration

Table 4 DSC curve characteristics and kinetic parameters of uncatalysed HTPB-IPDI reaction at different heating rates

No.	Heating rate/ °C min^{-1}	T_i/°C	T_s/°C	T_f/°C	E/kJ mol^{-1}	ln$A$
1	4	60	120	210	69.48	15.28
2	5	60	130	210	72.97	16.15
3	8	60	134	220	74.92	16.72
4	10	60	138	220	76.65	17.09
5	15	80	146	225	80.61	18.19

tion could be observed without the *KC* correction [25]. From similar plots of E *vs.* ln$A$, the *KC* corrected E value was determined in each case of HTPB-IPDI cure reaction, by extrapolation to the reference value of ln$A$=16.15 and the results are included in Table 3 from which it can be seen that after the *KC* correction, E is in the expected trend of lower values for all the catalysed reactions. After the normalisation, the E values show a systematic decrease with increase in the catalyst concentration which is graphically represented in Fig. 3. The best-fit curve follows an exponential relation between *KC* corrected E and the catalyst concentration, c, as:

$$E = 58.43 + 10.81e^{-c/0.008095} + 2.592e^{-c/0.6601}$$

The exponential relationship is an indication of the high propensity of the cure reaction for catalysis by FeAA.

Conclusions

The cure reaction of HTPB with IPDI in presence of FeAA catalyst follows second order reaction kinetics. The activation energy normalised for the changes in pre-exponential factor by kinetic compensation correction showed a clear dependency on the catalyst concentration. The exponential nature of *E vs.* catalyst concentration is indicative of the high propensity of the HTPB-IPDI cure reaction for catalysis by FeAA. The trend followed by DSC cure reaction temperatures and the normalised activation energy values as a function of catalyst concentration is similar, implying interrelation between these two parameters and the significance of Arrhenius activation parameters in the study of the cure reaction of the resin.

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