

DSC STUDY ON THE EFFECT OF ISOCYANATES AND CATALYSTS ON THE HTPB CURE REACTION

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Abstract

The urethane forming cure reactions of hydroxyl terminated polybutadiene (HTPB) binder with three different isocyanate curatives, viz., toluene diisocyanate (TDI), isophorone diisocyanate (IPDI) and 4,4'-methylene bis(cyclohexyl isocyanate) (MCHI), were investigated by differential scanning calorimetry (DSC). The effect of two cure catalysts, viz., dibutyl tin dilaurate (DBTDL) and ferric tris-acetylacetonate (FeAA) on the cure reactions was also studied. Cure kinetics was evaluated using the multiple heating rate Ozawa method. The reactivities of the three isocyanates and catalytic efficiencies were compared based on the DSC reaction temperatures, activation energies and rate constants. Viscosity build-up in these systems at isothermal temperature was also studied and compared with the results from DSC.

Keywords: cure kinetics, DSC, HTPB, Ozawa method, viscosity build-up

Introduction

HTPB liquid prepolymers find extensive application as binders in composite solid propellants [1, 2]. The binder imparts dimensional stability and structural integrity to the propellant grain and also acts as fuel during combustion. The hydroxyl functional groups of HTPB undergo stoichiometric urethane reaction with isocyanates to form the polyurethane network which provides a matrix for the inorganic oxidiser and metallic fuel ingredients and imparts superior mechanical properties to the propellant. Conventionally toluene TDI is used as a curative for HTPB. Urethane formation is a fairly rapid reaction with TDI. Since this limits the useful pot life of the propellant, attempts have been made to decrease and control the rate of the cure reaction of HTPB with TDI [3]. Aliphatic IPDI and MCHI which are lesser reactive than TDI are preferred in propellant formulations where a high pot life of the propellant slurry is needed for processing big size grains [4]. A knowledge of the rate and kinetics of cure of the binder with various curatives is of utmost importance in estimating the pot life and thus the processability of the propellant slurry.

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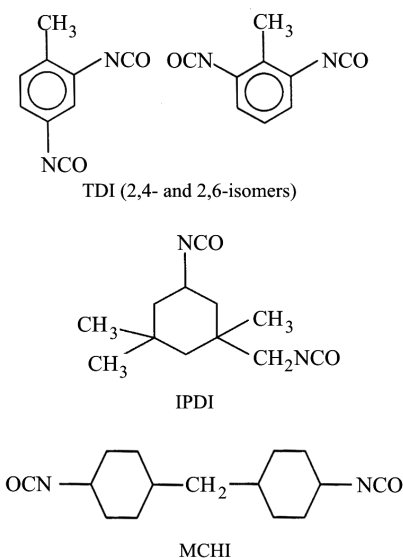
Kinetic investigations are one of the most important applications of thermal analysis. Thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are widely reported in evaluation of kinetic parameters. The DSC technique finds more applicability since almost all reactions produce or consume heat. Curing is an exothermic process and DSC has been extensively employed to study the cure reactions in polymers [5–7]. The cure reaction of HTPB with various curatives has been investigated by several workers using various techniques [8–21], with relatively more literature available on solution kinetics of the urethane formation. Reports on the use of DSC in the study of HTPB cure is limited [22].

In this study, curing of HTPB with three isocyanate curatives generally employed in composite propellants, viz., TDI, IPDI and MCHI, is studied using DSC. Reactions are carried out in uncatalysed condition as well as in presence of catalysts. Viscosity build-up in the different systems is also measured simultaneously and compared with the results from the thermoanalytical DSC method.

Experimental

Materials

HTPB resin was manufactured at VSSC, by the free-radical polymerisation of butadiene using hydrogen peroxide as initiator. The important properties are: hydroxyl value=42.5 mg KOH/g, $M_n=2600$, viscosity=5500 cPs (at 30°C). TDI, IPDI and MCHI were obtained from commercial sources and used as such after determining the purity by *n*-butyl amine titration. FeAA and DBTDL were also procured commercially. The structures of the three curatives are shown in Scheme 1.



Scheme 1 Structures of isocyanate curatives

Cure studies

HTPB and the curative (both cooled to 5°C) were mixed in 1:1 equivalent ratio with a catalyst concentration of 0.1% by mass of the resin. ~20 mg of the mixture was taken in aluminium pans and subjected to DSC analysis in a TA Instruments DSC 2920 in nitrogen atmosphere. The DSC cell was cooled to 5°C using a TA Instruments refrigerated cooling system (RCS) prior to initiating the temperature program. Heating rates were varied for determining the kinetics by Ozawa method [23]. FTIR spectra were recorded on a Perkin Elmer Spectrum GXA FTIR spectrometer using ATR accessory.

Cure kinetics

The multiple heating rate Ozawa method [23] was used to calculate the kinetic parameters, viz., activation energy 'E' and pre-exponential factor 'A'. The reactions were conducted at four different heating rates, viz., 2.5, 5.0, 7.5 and 10.0°C min⁻¹. A plot of log (heating rate) vs. 1/T_m (where T_m is the peak maximum in K) gave a straight line with slope equal to -E/2.19 R (where R is the gas constant=8.314 J mol⁻¹ K⁻¹). The pre-exponential factor

$$A \text{ (in min}^{-1}\text{)} = \phi E e^{E/RT} / RT^2,$$

where ϕ is the heating rate employed [24]. Rate constants were calculated using the Arrhenius equation $k = Ae^{-E/RT}$.

Viscosity build-up

Viscosity build-up in the resin mixtures (1:1 equivalents of HTPB and the isocyanate) were measured at fixed time intervals using a Brookfield microviscometer DV-RV II + with spindle number 14 and speed of 50 rpm.

Results and discussion

DSC cure

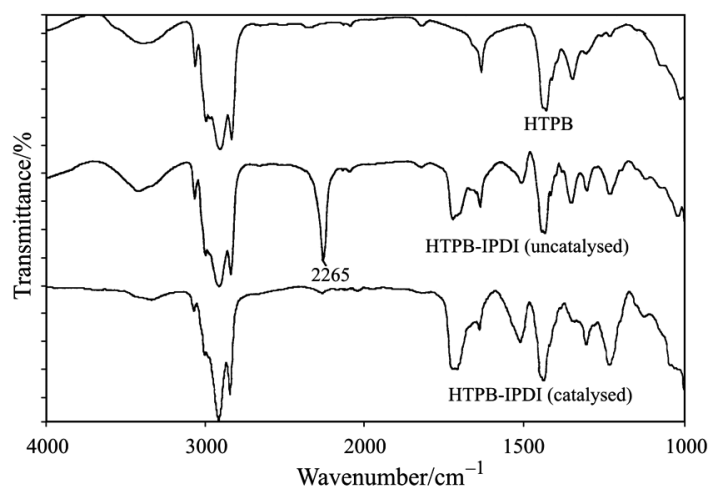
Table 1 lists the initial (T_i), peak (T_s), and final (T_f) temperatures, temperature interval, and enthalpies of uncatalysed and catalysed cure reactions at a heating rate of 5°C min⁻¹. Cure temperatures and reaction interval can be considered as an indicator of reactivity. Based on cure temperatures, reactivities for the uncatalysed reactions are in the order HTPB-TDI > HTPB-MCHI > HTPB-IPDI. Aromatic isocyanates are known to be more reactive than aliphatic groups due to the electron-withdrawing effect of the benzene ring. The cure temperature interval (T_f-T_i) is in the order HTPB-TDI < HTPB-IPDI ≥ HTPB-MCHI. The enthalpy values, ΔH, were low, being ΔH ≈ 5.0 J g⁻¹ for the TDI, 12 J g⁻¹ for the IPDI and 16 J g⁻¹ for the MCHI cured reactions. Urethane reactions are reported to be only moderately exothermic [25]. FTIR spectra were recorded after DSC cure to ensure whether curing was completed. Figure 1 shows the IR spectra of HTPB resin, and of the urethanes formed after heating in

Table 1 Reaction temperatures and enthalpies of the cure reactions

Catalyst	System	$T_i/^\circ\text{C}$	$T_s/^\circ\text{C}$	$T_f/^\circ\text{C}$	$T_f-T_i/^\circ\text{C}$	$\Delta H/\text{J g}^{-1}$
Nil	HTPB-TDI	18	60	120	102	5
	HTPB-IPDI	60	128	212	152	11
	HTPB-MCHI	50	118	210	160	16
FeAA	HTPB-TDI	15	55	110	95	28
	HTPB-IPDI	15	48	115	100	40
	HTPB-MCHI	18	58	121	103	34
DBTDL	HTPB-TDI	4	76	130	126	10
	HTPB-IPDI	16	56	146	130	24
	HTPB-MCHI	10	58	132	122	24

the DSC cell in uncatalysed and catalysed (FeAA) conditions. Absorption at 2258 cm^{-1} characteristic of isocyanate was present in all the samples implying that quantitative consumption of the reactants had not occurred and hence curing was incomplete. This can be expected, since HTPB curing process is known to be slow, requiring several days under isothermal conditions (at 60°C) during propellant manufacture.

In order to bring about completion of cure during the span of the DSC experiment, cure catalysts were employed. The FTIR spectra of samples cured in presence of DBTDL and FeAA showed absence of isocyanate absorption and hence complete conversion of the hydroxyls to urethane. Both the catalysts have lowered the cure reaction temperatures, the extent of lowering being greater for the aliphatic isocyanate (IPDI and MCHI) cured reactions than for the reaction with aromatic TDI. ΔH values have been enhanced in the catalysed reactions. This is clearly seen in Fig. 2 showing the superimposed DSC cure exotherms of uncatalysed and FeAA-catalysed HTPB-IPDI reaction.

**Fig. 1** IR spectra of HTPB and urethanes formed in absence and in presence of catalyst

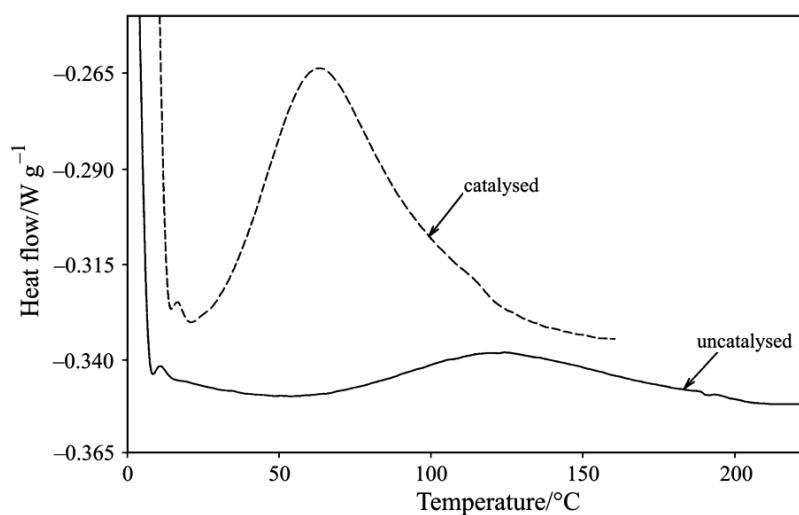


Fig. 2 DSC curve exotherms of uncatalysed and FeAA-catalysed HTPB-IPDI reaction

The HTPB-TDI system showed erratic behaviour in presence of the catalysts. Here, the DSC curves did not cause the expected lowering in reaction temperatures. However, from practical experience it is known that this reaction is a very fast one. It can be presumed that the dynamic DSC method is not appropriate in the study of such reactions, where a considerable amount of reaction has already occurred before commencement of the DSC experiment, and thus the DSC curve is not representative of the actual cure. It is more meaningful to compare the results of the IPDI and MCHI cured systems. Between the two catalysts, FeAA caused greater lowering in reaction temperatures and temperature interval, and greater enhancement in ΔH values, than DBTDL indicating that FeAA is a better catalyst in HTPB cure reactions with the reactivity of IPDI > MCHI.

Cure kinetics

The kinetics of the uncatalysed cure reactions were not evaluated since they were found to be incomplete. The values for activation energy, pre-exponential factor and rate constant at 60°C (the temperature of actual propellant cure) for the catalysed systems were computed using the Ozawa method and are given in Table 2. E values were in the range of 53–61 kJ mol⁻¹ for FeAA-catalysed and 35–48 kJ mol⁻¹ for DBTDL-catalysed cure reactions of HTPB. Almost similar values have been reported by Singh *et al.* [17] (=39 kJ mol⁻¹) and by Kincal and Ozkar [15] (=44 kJ mol⁻¹) for uncatalysed curing of HTPB with TDI and IPDI respectively using other bulk curing methods.

E values are expected to be lower for reactions with higher rate constants. This is not observed in any of the four systems reported in Table 2. This could be because of the corresponding increase in A values, and can be explained based on kinetic compensation (KC) effect [22]. Therefore a comparison of reactivities based on E values is not feasible

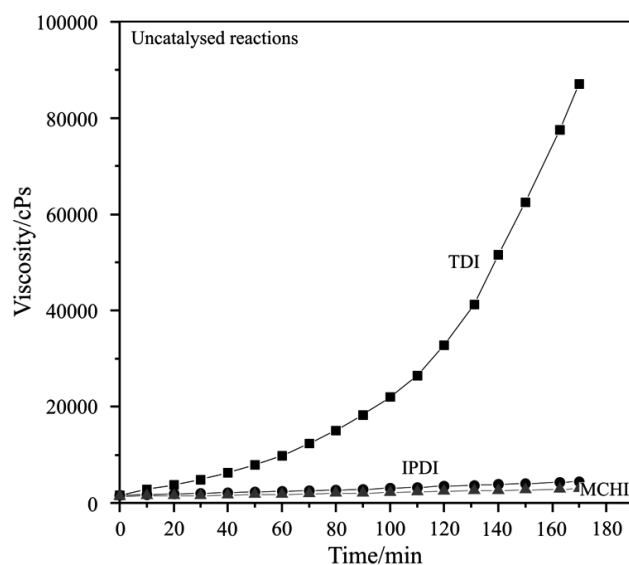
Table 2 Kinetic parameters of catalysed cure reactions

Catalyst	System	$E/\text{kJ mol}^{-1}$	A/s^{-1}	k (at $60^\circ\text{C})/\text{s}^{-1}$
FeAA	HTPB-IPDI	61.1	5.578 E7	1.444 E-2
	HTPB-MCHI	53.0	1.132 E6	5.462 E-3
DBTDL	HTPB-IPDI	35.1	1.654 E3	3.391 E-3
	HTPB-MCHI	47.9	2.232 E5	4.418 E-3

without applying a correction for KC effect. Comparison of the rate constants appear to be a more realistic approach in comparing reactivities. Rate constants of FeAA-catalysed HTPB cure reactions were higher than of DBTDL-catalysed reactions. Reactivity of IPDI>MCHI (in presence of FeAA) and MCHI>IPDI (in presence of DBTDL).

Viscosity build-up

In the uncatalysed systems, the viscosity was measured at fixed time intervals at 60°C . Viscosity build-up was most rapid in the case of the fastest reacting TDI, followed by IPDI and MCHI which showed almost similar behaviour. In catalysed system, curing was conducted at 30°C since the samples were found to gell within 15 min at 60°C . The order of viscosity build-up was different in the uncatalysed and catalysed reactions. Figures 3 to 5 show the pattern of viscosity build-up in uncatalysed, FeAA-catalysed and DBTDL catalysed systems respectively. In presence of FeAA, reactivity of curatives was in the order IPDI>TDI=MCHI, while in presence of DBTDL, the order was TDI>MCHI>IPDI, which agrees with the results from DSC analysis.

**Fig. 3** Viscosity build-up in uncatalysed HTPB-IPDI cure reaction

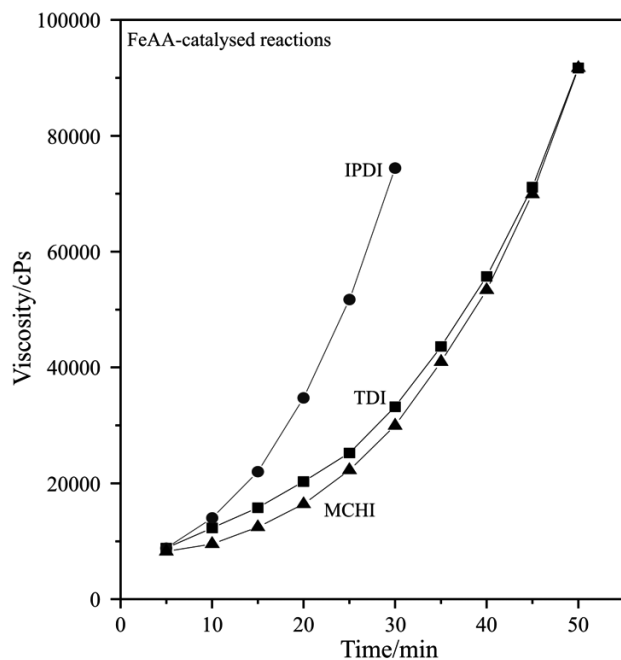


Fig. 4 Viscosity build-up in FeAA-catalysed HTPB-IPDI cure reaction

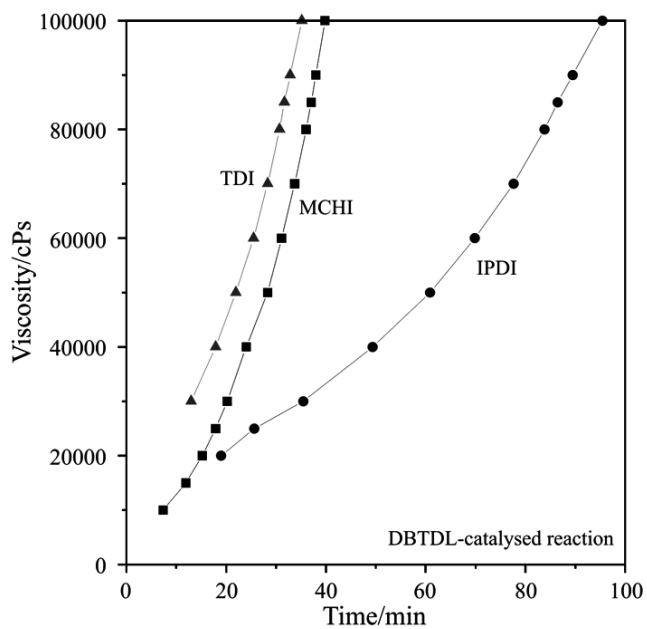


Fig. 5 Viscosity build-up in DBTDL-catalysed HTPB-IPDI cure reaction

Conclusions

HTPB cure reactions by DSC required the presence of a catalyst for complete conversion. The reactivities of the three isocyanates towards HTPB were compared based on DSC phenomenological data (reaction temperatures and temperature interval), and on kinetic data (activation energy and rate constant). DSC did not give accurate results for the fast HTPB–TDI cure reaction. The rate constants provided a good index of reactivity, according to which the reactivities of IPDI>MCHI in presence of FeAA, and MCHI>IPDI in presence of DBTDL. FeAA appeared to be a better catalyst than DBTDL in HTPB cure reactions. Viscosity build-up data showed the same trend of isocyanate reactivity as observed from DSC data, thus endorsing the applicability of DSC (with inherent advantages of speed and small sample size) as a reliable method for the study of HTPB cure reactions.

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