Curing kinetics of a rigid polyurethane foam formulation

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The curing kinetics of a typical commercial formulation used in the manufacture of rigid polyurethane foams has been studied. The adiabatic temperature rise method was used, taking into account corrections for heat losses. A polymeric isocyanate was reacted with a stoichiometric amount of a polyether polyol, using dibutyltin dilaurate (DBTDL) as catalyst. For DBTDL$<$2.6 mol m^{-3}, a strong inhibition of the catalyst took place, and the uncatalysed reaction played a major role. Second order kinetics gave a good fit for the whole conversion range. For DBTDL$>$2.6 mol m^{-3}, the catalysed reaction took place. Second order kinetics were applicable up to the gel point, but then the rate slowed down severely. A first order dependence on the initial catalyst concentration was observed in the pre-gel region. The kinetics are discussed in terms of a modified version of the Van der Weij's mechanism. The heat of reaction was 17.6 kcal/NCO equivalent.

Keywords Polyurethane kinetics; polyurethane foams; polyurethane reaction mechanism; polyurethane curing; adiabatic temperature rise

INTRODUCTION

Owing to their low apparent thermal conductivity, polyurethane rigid foams have a widespread use in insulation. The manufacture of a foam consists of several distinct steps: (a) mixing of the polyol, containing the catalyst, a surfactant and chlorofluorocarbon blowing agent, with the isocyanate; (b) creaming period, in which the temperature increase caused by the exothermic chemical reaction is sufficient to promote the activity of the blowing agent; (c) rising period, in which the agent evaporates raising the foam until a sufficient rigidity is reached and rising stops; (d) postcuring period. In order to model the foaming process the kinetics of the bulk polymerization must be available.

Few studies of bulk urethane reaction kinetics have been reported in the literature[1-6]. Most of them deal with reaction injection moulding formulations, and to our knowledge there is no reported study dealing with rigid foam formulations. There is, in fact, a significant difference between both kinds of formulations, which is the average functionality of reactants. Rigid foams are usually made with reactants (one or both) of high functionality, to attain a sufficient rigidity at a relatively low reaction extent. That is to say, the gel conversion for foaming is lower than for reaction injection moulding. This may have a bearing on the overall kinetics if diffusional steps are present in the reaction mechanism.

The aim of this paper is to analyse the curing kinetics of a typical commercial formulation used in the manufacture of rigid polyurethane foams. The suitability of reaction mechanisms proposed in the literature will be discussed.

METHOD

Measuring reaction kinetics

Adiabatic temperature rise has been reported as the most useful method for obtaining kinetic data on fast bulk polymerizing systems[4]. We have shown that the method can also be applied to reactions which are not very fast, if corrections for heat losses are taken into account[7]. The energy balance per unit mass is stated in an unspecified control volume containing the measurement point. It is written as:

$$c_p \mathrm{d}T_{\mathrm{exp}}/\mathrm{d}t = (-\Delta H)\mathrm{d}x/\mathrm{d}t - U(T_{\mathrm{exp}} - T_0) \qquad (1)$$

where c_p is the specific heat, $(-\Delta H)$ is the heat evolved per unit mass, both assumed constant (this is not a necessary hypothesis[4]), U is the global heat transfer coefficient per unit mass, x and T_{exp} are, respectively, the conversion and experimental temperature, measured at time t, and T_0 is ambient temperature.

The heat transfer coefficient, written as $U' = U/c_p$, may be obtained by integrating equation (1) for sufficiently long times, i.e. $t > t_1$, when $\mathrm{d}x/\mathrm{d}t \to 0$. It results:

$$\ln(T_{\mathrm{exp}} - T_0) = \ln(T_{\mathrm{exp1}} - T_0) - U'(t - t_1) \qquad (2)$$

The coefficient U' arises from the T_{exp} vs. t observed decay.

However, the adiabatic temperature T (temperature which would be measured in a true adiabatic reactor) verifies the following energy balance:

$$c_p \mathrm{d}T/\mathrm{d}t = (-\Delta H)\mathrm{d}x/\mathrm{d}t \qquad (3)$$

From equations (1) and (3) it results:

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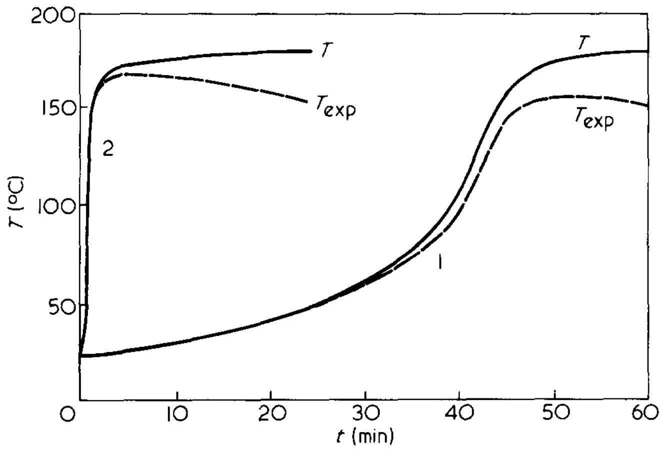

Figure 1 Experimental (dashed lines) and adiabatic (solid lines) temperature rises for different catalyst concentrations. Run 1: DBTDL = 2.17 mol m^{-3}, run 2: DBTDL = 6.22 mol m^{-3}

$$T = T_{\exp} + \int_0^t U'(T_{\exp} - T_0)\mathrm{d}t \qquad (4)$$

which enables the calculation of the adiabatic curve from experimental information.

The conversion is given by:

$$x = (T - T_0)/\Delta T_{\mathrm{ad}} \qquad (5)$$

where $\Delta T_{\mathrm{ad}} = (-\Delta H)/c_p$.

If *n*th order kinetics are proposed to fit the adiabatic curves,

$$\mathrm{d}x/\mathrm{d}t = A(1-x)^n \exp(-E/RT) \qquad (6)$$

a rearrangement of equation (3) leads to:

$$\ln k = \ln\left\{\frac{\mathrm{d}T/\mathrm{d}t}{\Delta T_{\mathrm{ad}}[1-(T-T_0)/\Delta T_{\mathrm{ad}}]^n}\right\} = \ln A - E/RT \qquad (7)$$

The *n* value which gives a correlation coefficient (c.c.) closest to 1 when making the linear regression is the one selected. *A* and *E* arise from the corresponding ordinate and slope.

EXPERIMENTAL

Materials

A typical formulation for rigid foams was selected. The polymeric isocyanate was a polymethylenepolyphenyl isocyanate (PAPI 135, Upjohn), with an average functionality = 2.7 and an equivalent weight of 133.5 g, as reported by the supplier. It was reacted with a polyether polyol based on sorbitol (NIAX LS 490, Union Carbide), with an OH value of 490 mg KOH/g polyol, a number average molecular weight equal to 550 g/mol (cryoscopy in dioxane) and a resulting average functionality equal to 4.8. The catalyst was dibutyltin dilaurate, DBTDL (D22 Union Carbide). All materials were used as received.

Regarding the polymeric isocyanate, it must be acknowledged that the molecular weight distribution may be fairly broad and the $-$NCO groups may not be all of equal reactivity. The same is valid for the polyether polyol. Thus, the reported kinetics will be associated with the average behaviour of reactive functionalities.

Procedure

The reactor was a tube of 15.5 cm length and 7 cm internal diameter, thermally insulated with polyurethane foam. Both reactants were added in stoichiometric amounts, at room temperature, together with a volume of catalyst necessary to give a concentration in the range 1–8 mol DBTDL/m^3 of final mixture. Mixing was carried out over 15 s with a motor-driven mixer, consisting of two propellers with 3 blades each, operating at 2200 rpm. A stopper with a copper–constantan thermocouple protruding from its centre was placed on the container. Its output was monitored with a data logger (Fluke 2200 B).

Energetics

The specific heats of reactants and the cured product were obtained with a Du Pont Thermal Analyzer provided with a d.s.c. pressure cell.

RESULTS

Kinetics

The dashed lines in *Figure 1* show the experimental temperature rises for two different catalyst concentrations. The solid lines correspond to the adiabatic rise, as calculated from equation (4). Obviously, the corrections are less significant for fast reaction rates. *Figure 2* shows the calculation of the heat transfer coefficient, *U'*, for run 1 depicted in *Figure 1*. An excellent linear regression could always be obtained.

Adiabatic temperature rises were regressioned with an *n*th order kinetic expression. For low catalyst amounts, i.e. DBTDL < 2.5 mol m^{-3}, second order kinetics fitted the whole conversion range with a high correlation coefficient. For high catalyst amounts, i.e. DBTDL > 3 mol m^{-3}, second order kinetics suitable only in the 0–0.4 conversion range. When conversions became greater than 40%, the rate slowed down severely. *Figure 3* shows a second order regression for two typical runs.

An estimation of the gel conversion may be obtained by assuming the average functionalities of reactants to be the

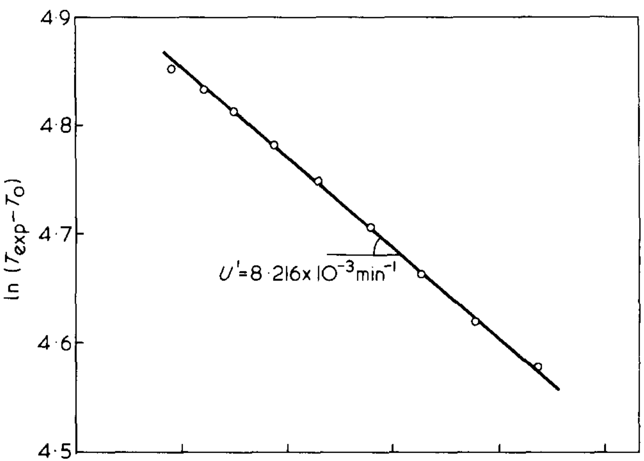

Figure 2 Experimental temperature decay for run 1 depicted in *Figure 1*

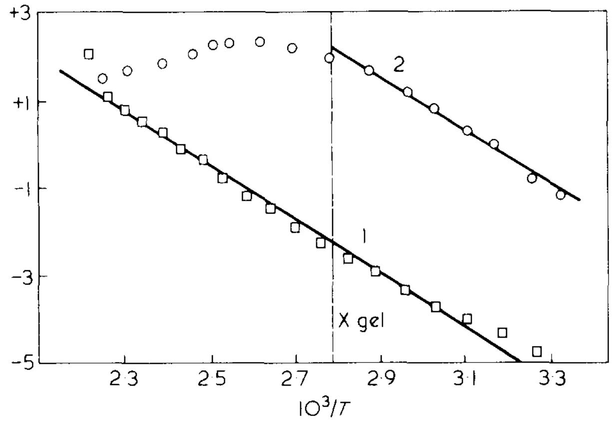

Figure 3 Second order kinetic regression for two typical runs. Run 1: DBTDL = 2.17 mol m^{-3}, run 2: DBTDL = 6.22 mol m^{-3}

Table 1 Kinetic parameters in the 0–0.4 conversion range

Run	DBTDL (mol m^{-3})	*E* (kcal mol^{-1})	*A* (min^{-1})	c.c.
1	1.20	10.2	1.07×10^5	0.999
2	1.69	10.0	7.34×10^4	0.996
3	2.17	7.0	1.63×10^3	0.992
4	2.17	9.7	6.98×10^4	0.997
5	2.71	6.1	1.18×10^3	0.995
6	3.13	11.2	1.15×10^7	0.997
7	3.61	12.2	9.04×10^7	0.998
8	6.22	12.8	6.80×10^8	0.997
9	7.77	14.3	5.14×10^9	0.994
10	7.77	15.5	4.36×10^{10}	0.997
11	7.77	14.0	4.24×10^9	0.995

same on number and weight bases (i.e., reactants have narrow distribution of functionalities). In this case[8],

$$x_{gel} = 1/\{(2.7-1)(4.8-1)\}^{1/2} = 0.39 \tag{8}$$

An approximate experimental gel point was obtained by pulling gently on the thermocouple during reaction, and quoting the temperature value at which the thermocouple resists movement. Several runs gave x_{gel} values in the range 0.35–0.40, in good agreement with the theoretical prediction. Thus, reported average functionalities are adequate for the prediction of gelation.

From the gel conversion value, it may be stated that at high catalyst concentrations the rate slows down in the post-gel period.

Table 1 shows the kinetic parameters arising from different runs, when fitted to a second order expression in the 0–0.4 conversion range. The fitting was excellent as shown by the high correlation coefficients. The dependence of the specific rate constant on the catalyst concentration is masked by the variations of the activation energy among different runs. If an average value, $\bar{E} = 10.7$ kcal mol^{-1} is taken, and the specific rate constants recalculated, the behaviour plotted in *Figure 4* is obtained. The specific rate constant does not depend on the catalyst concentration in the range 0–2.6 mol m^{-3}, and then increases linearly with concentration up to 8 mol m^{-3}. Thus, the following expression provides a rough fit for all kinetic runs in the 0–0.4 conversion range:

$$dx/dt = A(c)\exp(-10.7/RT)(1-x)^2 \tag{9}$$

with $A(c) = 2.0 \times 10^5$ min^{-1} for c(DBTDL) < 2.6 mol m^{-3}, and $A(c) = 2.0 \times 10^5$ min^{-1} $+ 0.936 \times 10^7(c - 2.6)$ min^{-1} m^3/mole DBTDL, for c(DBTDL) $\geqslant 2.6$ mol m^{-3}.

As previously pointed out, for $c < 2.6$ mol m^{-3} the regression is valid for the whole conversion range. For $c > 2.6$ mol m^{-3} and $x > 0.4$, no simple potential model enabled the matching of experimental curves. Instead, the following empirical expression fitted the kinetics for every catalyst concentration:

$$dx/dt = A(c)\exp(-E/RT)[1 - R(x)x]^2 \tag{10}$$

where $A(c)$ and E take the same values as in the pre-gel region, and

$$\begin{array}{ll} R(x) = 1\ , & x \leqslant 0.40 \\ R(x) = 1.292 - 17.2\,(0.65 - x)^3\ , & 0.40 < x \leqslant 0.684 \\ R(x) = 1.913 - 0.913x\ , & 0.684 < x \leqslant 1 \end{array}$$

The fact that $R(x) > 1$ makes the reaction rate decrease markedly after the gel point.

Energetics

The specific heats of reactants and cured products showed a slight linear increase with temperature, the difference between reactants and cured products being less than 10%. An average value of $c_p = 0.427$ cal/g °C was taken, in agreement with values given by Modern Plastics Encyclopedia[9] for cast polyurethanes.

The adiabatic temperature rise was $\Delta T_{ad} = 166$°C, varying in a ±6% range for different batches of reactants.

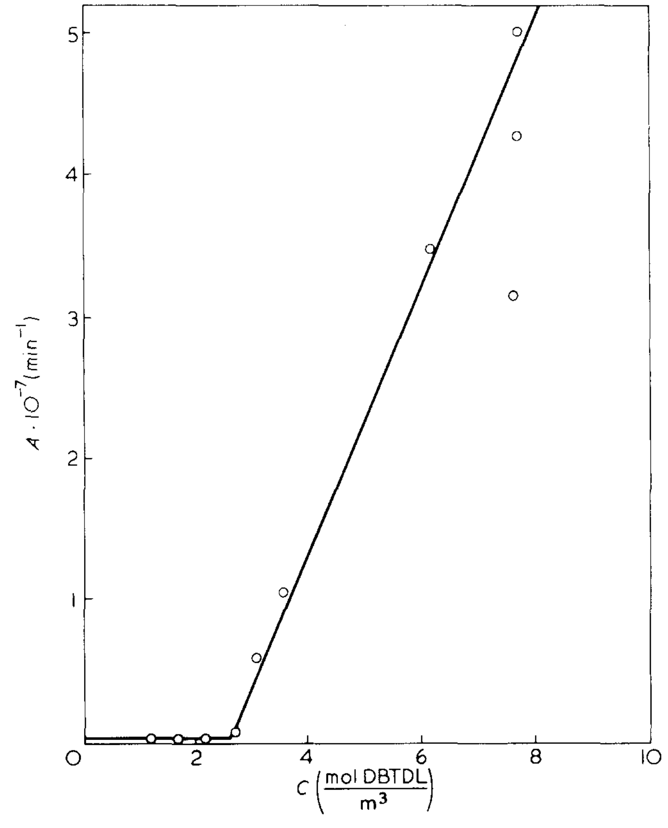

Figure 4 Influence of the catalyst concentration on the specific rate constant, for an average activation energy, $\bar{E}$ = 10.7 kcal mol^{-1}

The reaction heat is given by:

$$(-\Delta H)=c_p\Delta T_{\mathrm{ad}}=71\ \mathrm{cal/g}=17.6\ \mathrm{kcal/NCO\ equivalent}$$

DISCUSSION

Analysis of results plotted in *Figures 3* and *4* leads to the following statements:

(a) For DBTDL <2.6 mol m^{-3} the experimental reaction rate was low and not dependent on the catalyst concentration. An uncatalysed reaction is probably taking place. The second order kinetics are in agreement with previous reported results[1-3,6]. The same holds for the range of activation energies shown in *Table 1*[3]. In order to justify the low performance of the catalyst in this range, the occurrence of a strong inhibition reaction may be proposed. In general, any impurity leading to a stable pentacoordinated Sn-complex inhibits the catalyst. This was shown to be the case when acetic acid was present in urethane formulations[10]. The nature of the inhibitor present in our commercial formulations could not be ascertained.

(b) The catalytic reaction taking place at DBTDL >2.6 mol m^{-3} showed a linear increase of rate with catalyst concentration. For DBTDL $=4.7$ mol m^{-3}, the catalytic rate is one hundred times greater than the uncatalysed one. When the gel appears the observed rate is no longer controlled by chemical reaction; diffusional restrictions as well as reaction between functionalities fixed in the gel should play a major role. It is worth pointing out that Lipatova[2] found a change in reaction order, from second to first, when passing through the gel point for the particular system under analysis. The reaction after the gel conversion was described as a structure-forming mechanism.

(c) The catalytic reaction before the gel point showed reaction order and activation energy values lying in the range of results reported for reaction injection moulding formulations[6]. Kinetic models reported by Baker and Holdsworth[11] and Richter and Macosko[6] enable us to explain the observed overall second order with respect to reactants and first order with respect to catalyst. However, it will be shown that a modification of the well-founded Van der Weij's mechanism can satisfactorily predict both his results and our observations. The following four steps are assumed to take place (step 4 is different from the one proposed by Van der Weij[10]):

$$(1)\ \mathrm{Y_2X_2Sn+ROH=Y_2X_2Sn.ROH}$$

$$(2)\ \mathrm{Y_2X_2Sn.ROH=(Y_2X_2SnRO)^-+H^+}$$

$$(3)\ \mathrm{(Y_2X_2SnRO)^-+R'NCO=(Y_2X_2SnR'NCOOR)^-}$$

$$(4)\ \mathrm{(Y_2X_2SnR'NCOOR)^-+H^+\rightarrow Y_2X_2Sn+R'NHCOOR}$$

If step (4) is assumed to be rate-determining, with steps (1), (2) and (3) in equilibrium, it results:

$$\begin{aligned}\mathrm{d(R'NHCOOR)}/\mathrm{d}t&=k_4\mathrm{(Y_2X_2SnR'NCOOR^-)(H^+)}\\&=k_4k_1k_2k_3\mathrm{(Y_2X_2Sn)(R'NCO)(ROH)}\end{aligned}$$

If k_1 is sufficiently low, $\mathrm{(Y_2X_2Sn)\rightarrow(Y_2X_2Sn)_0}$, and a first order dependence on the initial catalyst concentration is obtained. An overall second order with respect to reactants results from the proposed mechanism.

However, it may be shown that experimental observations reported by Van der Weij[10], for the dibutyltin diacetate catalysed reaction of phenyl isocyanate with methanol, in dibutyl ether at 25°C, are fitted with the proposed mechanism when step (3) is rate-determining. An overall 1.5 reaction order is obtained. It is worth pointing out that studies of bulk urethane reaction kinetics lead to overall reaction orders varying from 1.5 to 2, at constant catalyst concentrations[6]. Also, the order was found to increase from 1.5 to 2 with increasing temperature[6]. This may be explained with the proposed model, by a change in the nature of the rate-determining step.

Regarding the experimental value of the heat of reaction per NCO equivalent, it is consistent with previous reported values for RIM formulations[4,6].

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