

Sequential Nature of the Exothermic Reactions Leading to the Formation of Flexible Polyurethane Foams

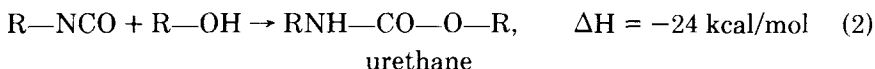
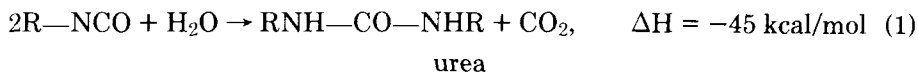
P. VAN GHELUWE, *National Research Council Canada, Industrial Materials Research Institute, 750 Bel-Air, Montreal, Quebec, H4C 2K3*, and
J. LEROUX, *Union Carbide Canada Ltd., 10455 Metropolitan Blvd., Montreal East, Quebec, H1B 5K8, Canada*

Synopsis

The exotherms of the reactions leading to the formation of polyurethane foams were measured. The inflection points of the exotherm curves were made evident by continuous differentiation with respect to time. The position and magnitude of the inflection points demonstrated the sequential nature of the reactions. The effects of the functionality of the polyol, the concentrations of the tin and amine catalysts, and the silicone surfactant are discussed.

INTRODUCTION

The production of flexible polyurethane foams rests on a delicate balance in the timing of two types of reactions. One results in the blowing of the liquid components into a foam while the other gels the mass. One of the interesting features of such a rising foam is the exothermic nature of the process. The heat is liberated by the initial reactions of the isocyanate with the water and then with the polyols¹:



Reaction (1) is responsible for the blowing of the foam by virtue of the carbon dioxide generated. Through polyurea formation, the initial viscosity buildup is accomplished. Reaction (2) then forms polyurethanes and leads to the gelling of the cellular structure. The urea and urethane groups will further react with the excess isocyanate usually introduced in these formulations and consolidate the structure through crosslink formation.

Early measurements of initial rates of temperature rise were found of interest for characterizing the reactivity of different polyol types and their sensitivity to catalyst variation.² A recent report³ correlated the temperature rise with the reaction sequence and the physical phenomena occurring during the foam rise. The conclusion was that no polyurethane was formed during the first 75% of the rise. However, the conditions required for accurate temperature measurements in these cellular systems were only later correctly defined.^{4,5} Parallel to these temperature studies, another approach provided by the BB test⁶ allows an un-

derstanding of the importance of the blowing reaction relative to the development of cell wall strength as a function of time. By varying the initial temperature of the reactants and the catalyst ratios, a balance suitable for the process can be found between both reactions.

The advent of computers in laboratories also generated new insight into the foaming process. Theoretical models attempted to predict the density and temperature at full rise of the foam block.⁷ Other groups undertook studies with the use of sophisticated instrumentation⁸ or by interfacing the standard Fluidyne Instrument⁹ with a small computer to obtain reactivity profiles.¹⁰

This work is a reexamination of the information provided by the exotherm. Many curves of temperature vs. time are presented in the literature,⁸ but, to our knowledge, have not been exhaustively analyzed. A close examination of each of these curves reveals the presence of inflection points which seem to be typical of the particular system or formulation involved. Thus our aim is to accurately characterize these exothermic curves with the aid of the new means we describe.

EXPERIMENTAL

Apparatus

A schematic of the setup is given in Figure 1. The chromel-constantan thermocouple wires are connected to a digital thermometer (Omega Engineering, Model 199) having an internal ice-point compensator. The analog output, linear in $\text{mV}/^{\circ}\text{C}$, is fed to a differentiating circuit capable of effecting the derivative with respect to time (dT/dt). The resulting two signals are directed to a two-pen recorder, where both are reproduced simultaneously. Beforehand, these two output voltages can be calibrated so that the charts are scaled in $^{\circ}\text{C}$ and in $^{\circ}\text{C}/\text{s}$ for the exothermic and derivative curves respectively. A typical recorder trace is presented in Figure 2. The relevant exothermic parameters can be extracted from the curves in the manner illustrated and are defined in the caption.

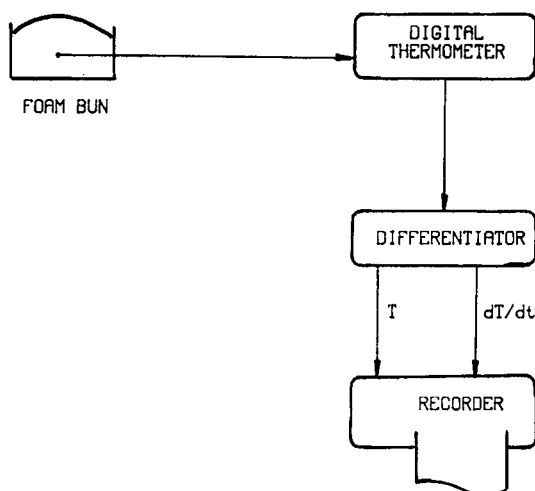


Fig. 1. Diagram of temperature and temperature differential measuring apparatus.

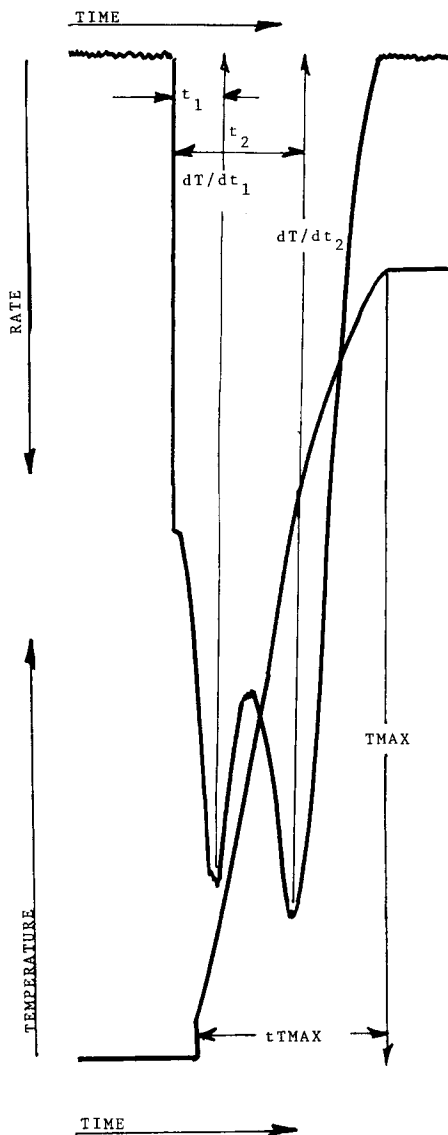


Fig. 2. Exothermic parameters obtained from the recorder chart: T_{max} = maximum temperature attained overall ($^{\circ}\text{C}$); $t_{T_{max}}$ = time required to attain this maximum (s); dT/dt_1 , dT/dt_2 = maximum rates of temperature rise of the two sequential reactions ($^{\circ}\text{C}/\text{s}$); t_1, t_2 = times required to attain these maxima (s).

In order to establish the reproducibility of the method, the exotherms of a standard four parts by weight water formulation were obtained from seven consecutive runs. The expanded temperature–rate-of-rise curves were then digitized. Statistical analysis using the Student t -distribution was then applied to the data and the computer regenerated two curves enclosing a 95% confidence interval (Fig. 3). It should be stressed that all conditions need to be kept constant within the set of runs such as, catalyst lots, reactant temperatures, operating procedures, etc.

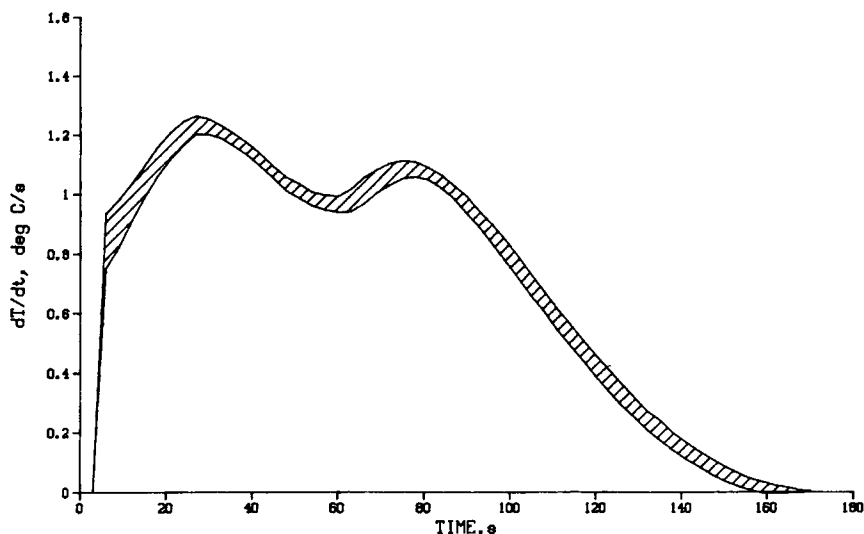


Fig. 3. The 95% confidence interval of temperature rate of rise vs. time.

The absolute error for the measurements on the time scale is estimated to be ± 1 s at the chart speeds normally used. Temperature is measured with a precision of $\pm 1^\circ\text{C}$ on the recorder chart calibrated from 0°C to 200°C . A calculation of the absolute error on the measurement of rate of temperature rise yields a value of 0.04°C/s . Using the Student t data of Figure 3, the spread of the 95% confidence interval is found to be 0.06°C/s at the peak rates leading to an average error of 0.03°C/s .

Materials and Procedure

Two commercial polyols were used in this study. Polyol 1 is NIAX® Polyol 16-46 (Union Carbide Canada Ltd.), a secondary hydroxyl end-terminated polyether triol. Polyol 2 is NIAX® Polyol 12-48 (Union Carbide Corp.), a 75-mol % primary hydroxyl end-capped polyether triol. Both polyether triols have a hydroxyl number of 47 ± 1 mg KOH/g and a residual water content of less than 0.02%. Toluene diisocyanate (TDI) obtained from BASF was used throughout and the material had an 80/20 ratio of the 2,4- and 2,6- isomers. The amine catalyst used in all the formulations was a 70% solution of bis(dimethylamino ethyl) ether in dipropylene glycol (NIAX® Catalyst A-1, Union Carbide Corp.), in conjunction with Union Carbide® Silicone Surfactant L-6202. Stannous octoate (T-9®, M&T Chemicals, Ltd.) was also used as catalyst.

For the purpose of obtaining an unreactive polyether containing no free hydroxyl end groups, polyol 1 was derivatized in two ways. In one case, polyol 1 (600 g) was mixed with acetic anhydride (78.8 g) and pyridine (61.0 g). The reaction was monitored by IR spectroscopy until completion was indicated by the total removal of the hydroxyl stretch from the spectrum at 3460 cm^{-1} . Excess reagents were removed at 50°C under high vacuum for 3 h. Complete removal of the pyridine was not achieved as indicated by the persistence of its strong odor.

TABLE III
Formulations with Varying Amounts of Stannous Octoate

	24	25	26	27	28	29	30	31	32	33	34
Polyol 1	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Polyol 2	—	—	—	—	—	—	—	—	—	—	—
Water	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Niax® Catalyst A-1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Surfactant L-6202	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Stannous octoate	0.15	0.20	0.25	0.30	0.35	0.40	0.15	0.20	0.25	0.30	0.40
TDI	48.6	48.6	48.6	48.6	48.6	48.6	48.7	48.7	48.7	48.7	48.7

In another preparation, polyol 1 (600 g, 0.5 eq) was reacted with phenyl isocyanate (61.9 g, 0.5 eq from Aldrich Chemicals) at 80°C for 6 h to yield a phenyl urethane capped polyether. The disappearance of the isocyanate stretch at 2250 cm^{-1} and of the hydroxyl stretch at 3460 cm^{-1} indicated that the reaction had gone to completion.

The procedure for the production of foaming samples suitable for temperature measurements has been reported previously.¹¹ A bare thermocouple wire (0.25 mm) is inserted in the container approximately 6 cm from the bottom. The arrangement is such that a major portion of the wire will be in contact with the rising foam. To insure immediate contact of the reacting liquid with the thermocouple, the junction is positioned at the center of a paper coffee cup itself placed at the center of the box. Once the mixing cycle has been completed, the reacting liquid mix is poured into the coffee cup until it overflows and the remainder is spread over the bottom of the box. The foam rises and the apparatus simultaneously records the temperature and the rate of temperature rise.

Heat loss is minimal and has been estimated for similar systems to be 2–6% at most.¹² Furthermore, because the reaction lasts less than 3 min and the fairly large foam bun (36 × 36 × 15 cm) has a low thermal conductivity, the reaction frame can then be considered to approximate adiabatic conditions. However, foams having a high proportion of open cells will exhibit a shorter maximum temperature plateau indicating a greater heat loss. Very low density foams will also afford reduced maxima, and the temperatures as well as the rates of temperature rise will tend to be lower than in reality due to the poor contact with the thermocouple junction.

Each polyol was reacted in a formulation where one of the components was varied. The contribution of the amine, the tin, and the water towards the buildup of the exotherm was thus obtained. These formulations where the indicated amount of TDI corresponds to 1.05 eq (105 index) relative to the active hydrogen compounds present in the resin part, are given in Tables I–IV.

RESULTS

Data Obtained from the Exotherm Curves

The trace of temperature vs. time yields two values characteristic of the system examined (Fig. 2). The maximum temperature attained within the foam [T_{max} (°C)] and the time it took to attain this plateau [$t_{T_{\text{max}}}$] are given in Tables V–VII together with the corresponding variables of the formulations.

TABLE IV
Formulations with Capped Polyol 1

	35	36
Acetate cap	100.0	—
Phenyl urethane cap	—	100.0
Water	4.0	4.0
Niax® Catalyst A-1	0.1	0.1
Surfactant L-6202	1.0	1.0
Stannous octoate	0.25	0.25
TDI	40.7	40.7

TABLE V
Effect of Water Concentration on the Exothermic Curve

Water (pbw)	Polyol 1						Polyol 2					
	2.0	3.0	4.0	5.0	6.0	6.6	3.0	3.5	4.0	5.0	6.0	6.6
T_{\max} (°C)	104	125	142	152	159	153	130	138	140	158	166	153
$t_{T_{\max}}$ (s)	253	181	138	128	116	132	234	168	135	120	123	132

TABLE VI
Effect of NIAX® Catalyst A-1 Concentration on the Exothermic Curve

NIAX® A-1 (pbw)	Polyol 1						Polyol 2					
	0.06	0.07	0.08	0.10	0.12	0.14	0.06	0.08	0.10	0.12	0.13	0.15
T_{\max} (°C)	142	140	142	141	142	144	143	143	140	143	144	146
$t_{T_{\max}}$ (s)	156	145	152	138	138	120	152	159	135	124	222	234

TABLE VII
Effect of Stannous Octoate Concentration on the Exothermic Curve

Stannous octoate (pbw)	Polyol 1						Polyol 2					
	0.15	0.20	0.25	0.30	0.35	0.40	0.15	0.20	0.25	0.30	0.40	
T_{\max} (°C)	133	138	141	146	147	148	140	143	140	146	144	
$t_{T_{\max}}$ (s)	170	155	138	126	110	98	152	152	135	119	123	

TABLE VIII
Exothermic Parameters for Capped Polyethers

	Phenyl urethane cap	Acetate cap
T_{\max} , (°C/s)	100	115
$t_{T_{\max}}$ (s)	483	224
t_1 (s)	29	23
t_2 (s)	—	—
dT/dt_1 (°C/s)	0.71	1.55
dT/dt_2 (°C/s)	—	—

The exothermic parameters obtained from the reactions in presence of the polyol derivatives are given in Table VIII. Only one peak exotherm was observed for both polyethers as indicated.

Data Obtained from the Derivative Traces

For each formulation, the values t_1 , t_2 , dT/dt_1 , and dT/dt_2 were obtained from the derivative curve. Plots of these parameters as a function of the component concentration are presented for each polyol in Figures 4–6.

Correlation of Exothermic Parameters with Rate of Rise Data

The rates of rise of the foam bun for several formulations were obtained with a Fluidyne Instrument (Fluidyne Instrumentation, Oakland, Calif.) and the values compared to the corresponding thermal parameters (Table IX). A plot of the maximum rate of temperature rise of the first exotherm (dT/dt_1) vs. the maximum rate of rise of the foam bun is illustrated in Figure 7.

DISCUSSION

The Significance of the Two Peak Exotherms

The fact that the exothermic curves (temperature vs. time) of water-blown polyurethane systems are not truly monotonous and exhibit slight inflection

TABLE IX
Comparison of the Foam Rate of Rise Data with the First Exotherm Parameters

Formulation	dT/dt_1 (°C/s)	t_1 (s)	t_{MRR}^a (s)	MRR ^b (in./min)
1	0.72	20	13	2.3
3	1.24	28	28	6.4
6	1.22	27	25	4.4
7	1.34	27	28	6.2
19	1.36	27	30	7.5
21	1.51	27	27	7.4
22	1.52	22	24	6.4
33	1.49	29	28	7.1

^a t_{MRR} = time to maximum rate of foam rise.

^b MRR = maximum rate of foam rise.

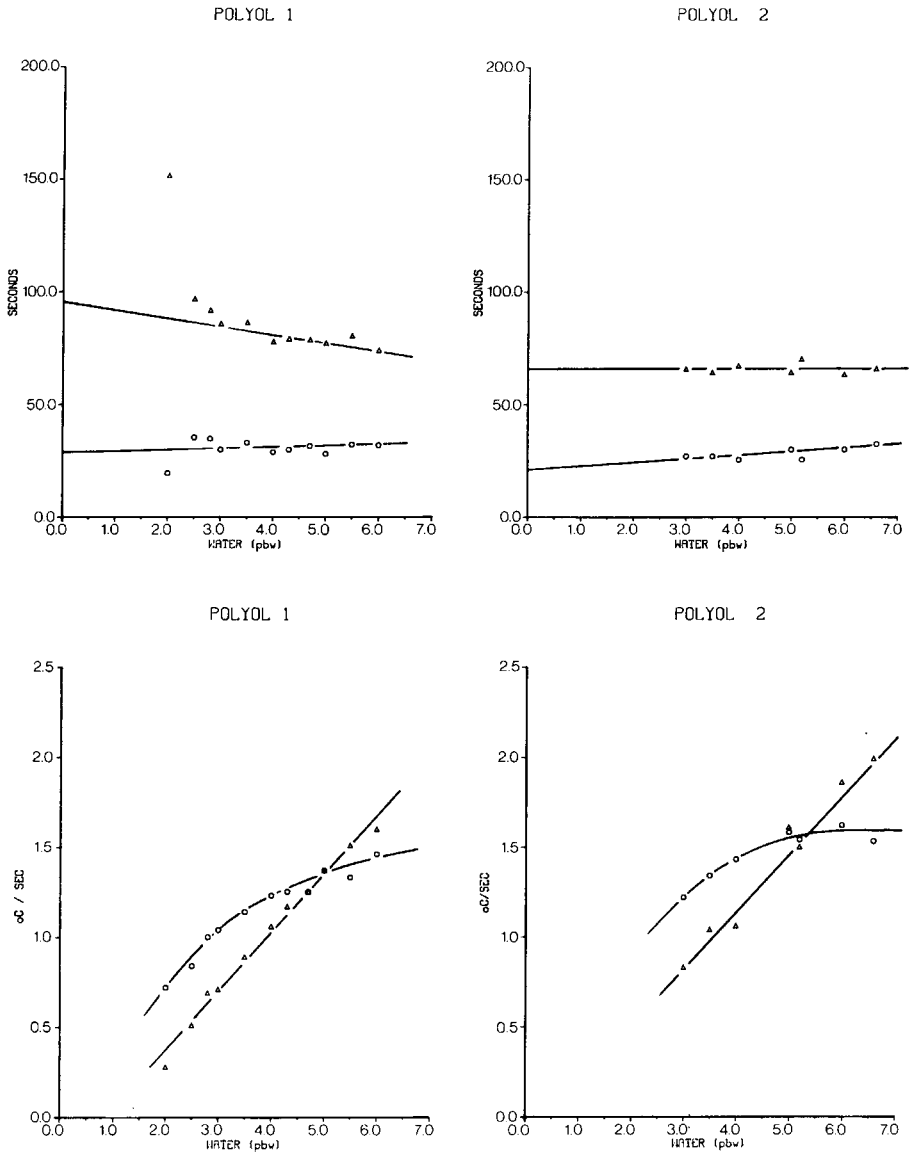


Fig. 4. Plots of exothermic parameters vs. water concentration: (O) t_1 , dT/dt_1 ; (Δ) t_2 , dT/dt_2 .

points has not been discussed to our knowledge. The technique applied here allows an exact positioning of the points of maximum temperature rise (t_1 and t_2) as well as an accurate evaluation of the maximum rate of rise (dT/dt_1 and dT/dt_2) for each of the individual exotherms of the whole curve.

The presence of two peak exotherms in the overall trace then stresses the sequential nature of the chemistry leading to polyurethane foam. Since two essential reaction steps are involved¹¹ during the process, it is evident that the first peak exotherm (t_1 and dT/dt_1) should correspond to the blowing reaction while the second surge in the exotherm (t_2 and dT/dt_2) can be related to the urethane-forming reaction. This assignment, although it is convenient, lacks rigor

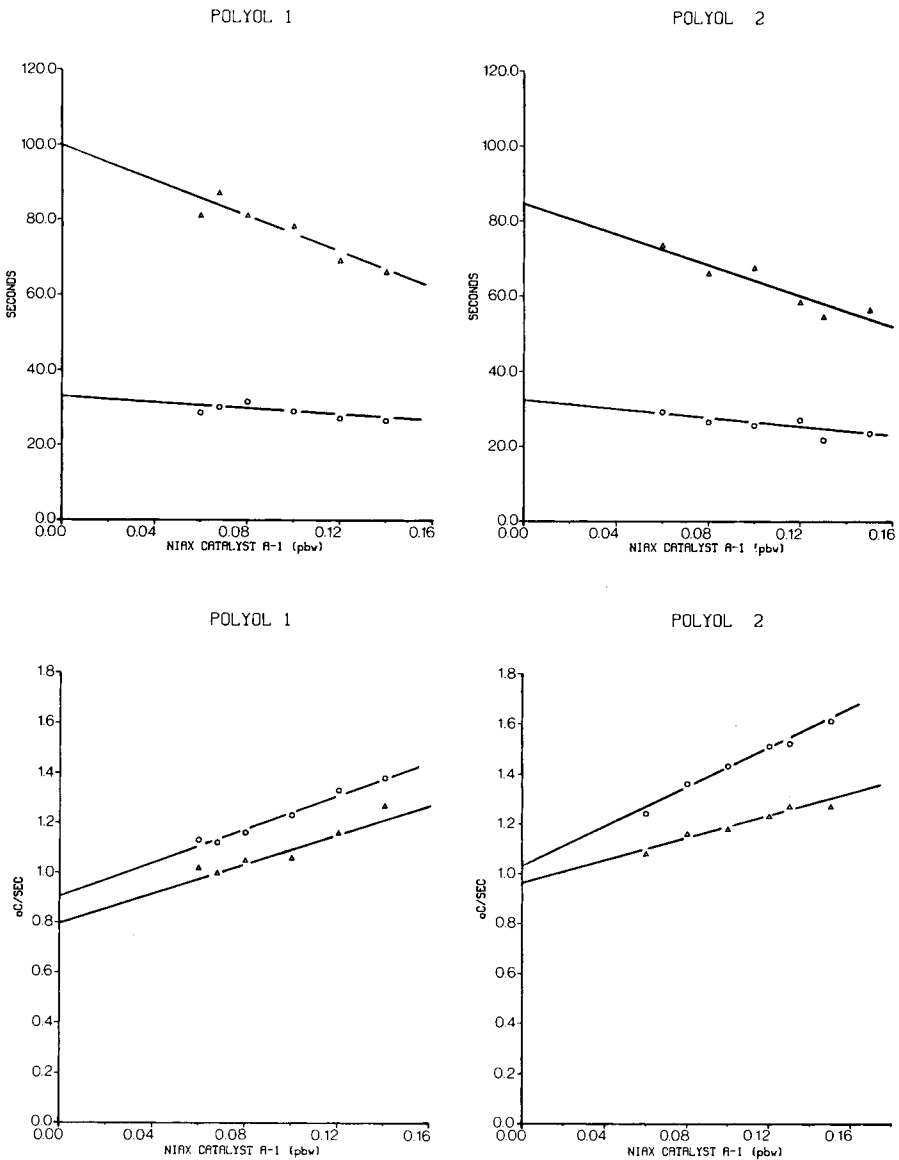


Fig. 5. Plots of exothermic parameters vs. amine concentration: (○) t_1 , dT/dt_1 ; (Δ) t_2 , dT/dt_2 .

in that both peaks in the derivative curve overlap to some extent. This is so because the activation energies of both reaction steps are of the same order of magnitude.¹³ From the process point of view, however, it is customary to distinguish the blowing step and the gelling step. A good correlation is observed in a comparison of the times at which the foam attains a maximum rate of rise (t_{MRR}) with the times at which the first exotherm attains a maximum rate of temperature rise (t_1) (Table IX). A plot of the maxima of both rates of rise (Fig. 7) also affords a fair correlation. Thus, higher values for dT/dt_1 , typical of a more reactive system, also correspond to higher values for the foam rate of rise. These particular features of the exothermic curves are thus coincident with the physical

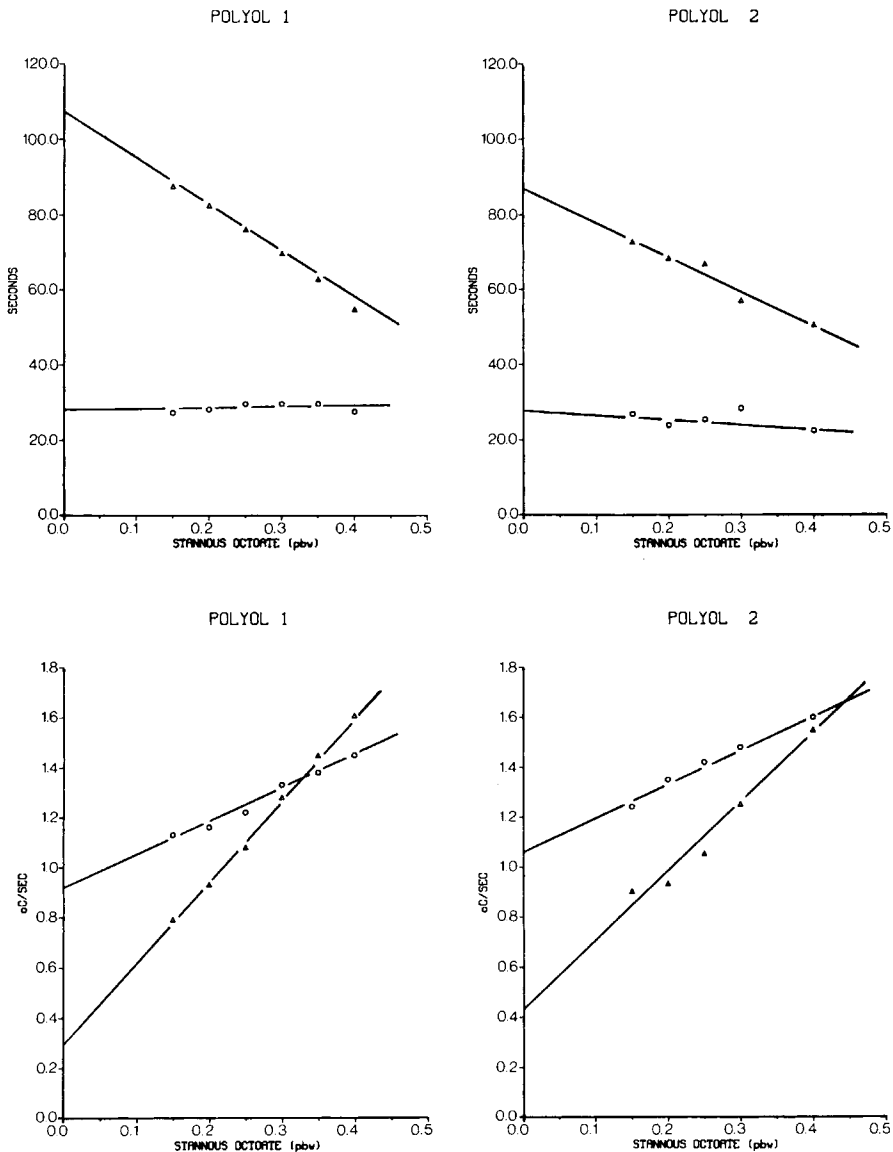


Fig. 6. Plots of exothermic data vs. stannous octoate concentration: (O) t_1 , dT/dt_1 ; (Δ) t_2 , dT/dt_2 .

parameters measurable on a rising foam lending support to the significance of this peak exotherm.

The occurrence time of the second peak exotherm (t_2) corresponds to the near completion (98–99%) of the rise of the foam bun as measured with the Fluidyne Instrument. At this time the rate of gelling attains a maximum and consolidation of the cellular structure begins. Foaming reactions performed with nonreactive capped polyethers did not exhibit the latter peak whereas the characteristics of the first peak exotherm remained similar (Table VIII). The rate of temperature rise with the phenyl urethane-capped polyether is slower than with un-

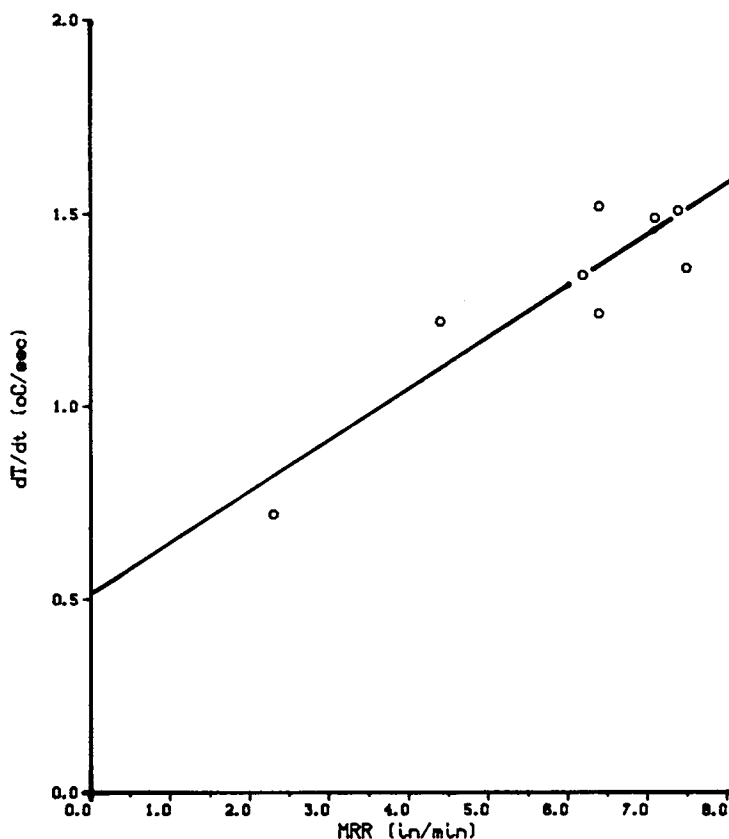


Fig. 7. Maximum rate of temperature rise of the first exotherm vs. the maximum rate of rise of the foam.

capped polyether triol, possibly because of the higher viscosity of the polyether derivative. On the other hand, the corresponding rate for the acetylated polyether was considerably higher. The remaining trace of pyridine is likely to be the cause by having further catalyzed the reaction of water with TDI.

The Effect of Water on the Exotherm

Water is introduced in urethane foam formulations primarily to allow expansion into a cellular structure, although it also leads to the formation of polyurea. The amount used will not solely afford a more vigorous blowing reaction but will also favor the gelling reaction (Fig. 4). The overall exotherm (Table V) resulting from these formulations reflects a more reactive system as the water concentration increases. Maximum temperatures within the foam increase and the times required to attain them get shorter. While dT/dt_1 for both polyols tapers off, dT/dt_2 related to the gelling reaction follows a linear progression. Why the temperature rate of rise of the expansion should reach a maximum, remains unexplained. However, the polyurea generated could participate as a cocatalyst in the urethane-forming reaction, accounting for the second relationship.

Both extremes of the water concentration range represent the limits for practical processing. In fact, low concentrations do not allow a sufficient buildup in the expansion rate whereas the other extreme, a high water concentration, will yield a foam of extremely low density. In each case, this has bearing on the temperature measurement. In the first case, broader dT/dt vs. t curves will be obtained, rendering less accurate the evaluation of the peak exotherm positions. This is evident in Figure 4, where t_1 and t_2 depart from linearity at concentrations below 3.0 pbw water. In the other case, low density foam will have extremely tenuous struts and a somewhat larger cell size. This is not conducive to maximum contact with the thermocouple junction and may in some cases lead to reduced rates of temperature rise. Reproducibility under these conditions will suffer.

Effect of Tin and Amine Catalysts on the Exotherm

The maximum temperatures attained within the foams increase with an increasing concentration of tin catalyst for both polyols. The times required to attain these maxima are also shorter. The maximum rates for the two peak exotherms also increase with the amount of tin catalyst. The slopes of dT/dt_1 and dT/dt_2 in Figure 6 are 1.34°C/s-pbw and 3.34°C/s-pbw , respectively; for polyol 1 and for polyol 2 they are 1.40°C/s-pbw and 2.74°C/s-pbw , respectively. Stannous octoate is thus seen to have a greater catalytic effect on the gelling reaction relative to the blowing step. The trend is seen for both polyols but the difference is not as marked with polyol 2. These observations thus support the assumption that stannous octoate is a predominantly gelling catalyst. In fact, the slopes for dT/dt_1 for both polyols are similar, it is only the slopes related to dT/dt_2 which vary. This difference is to be associated with the greater reactivity of polyol 2 caused by its primary hydroxyls, catalysis tending to have a lesser effect when the system is already very reactive.

With increasing concentrations of the amine catalyst, the maximum temperatures attained do not vary appreciably (Table VI). The maximum rate of the first exotherm for both polyols increase with an increase in the amine catalyst concentration. The second peak exotherm follows the same trend. The difference between the slopes of dT/dt_1 and dT/dt_2 for both polyols is not as great as in the case of tin. The values are, for polyol 1, 3.45°C/s-pbw and 3.13°C/s-pbw , respectively, for the blowing and gelling reactions, and 3.92°C/s-pbw and 2.14°C/s-pbw , for polyol 2. Thus, although NIAX® Catalyst A-1 is considered to be predominantly a blowing catalyst, its effect on both reactions is nearly equal with polyol 1. For polyol 2, the blowing rate reaction is much more affected relative to the gelling reaction (i.e., 3.92°C/s-pbw vs. 2.14°C/s-pbw).

Comparison of Two Polyols: Reactivity

The higher proportion of primary hydroxyl end groups in polyol 2 is expected to render the system in which it is included more reactive. All the parameters extracted from the temperature rate of rise curves are in agreement with this assumption. The maximum temperatures attained are always greater and occur at shorter times with polyol 2. If we look at the positions of the peak exotherms, t , one observes the same behavior for both polyols, but t_2 extrapolates to lower values for polyol 2. Similarly the maximum rates of rise of temperature increase;

dT/dt_1 and dT/dt_2 are consistently higher for the polyol containing primary alcohols. It is thus possible using the device to assess the overall reactivity of a polyurethane foaming system. The factors involved are easily segregated because their effect on either the expansion or the gelling steps is clearly evidenced. Ultimately, the correct equilibrium can easily be found between both steps in the reaction sequence.

Absolute Rates and Kinetics

To use this technique and the data it yields for obtaining absolute rate parameters would be hazardous. The overall reaction kinetics do not observe simple orders.¹² The complexity arises because of the many reactants involved and the possibility of autocatalysis by the products. Furthermore, because of the physical nature of the system and the heat gradients that are established, an adequate mathematical treatment would become extremely involved.

CONCLUSION

A method of analysis based on the continuous determination of the first derivative of the temperature vs. time curve of chemical reactions has been developed. With this novel exotherm characterization technique, the physical phenomena occurring during the formation of a polyurethane foam are now easily related to the chemistry involved. The relative importance of both the blowing and gelling steps can be assessed by their individual contribution to the overall exotherm. This in turn allows an adequate choice of formulation components and processing parameters. Although this approach to the reactivity of a system has been applied to the particular case of foaming polyurethanes, other vigorous thermosetting reactions could benefit from a closer examination by this technique.

References

1. G. Woods, *Flexible Polyurethane Foams, Chemistry and Technology*, Applied Science Publishers, London, 1982, p. 5.
2. A. J. Lowe, E. F. Chandley, H. W. Leigh, and L. Molinario, *J. Cell. Plast.*, **1**, 121 (1965).
3. G. R. Rossmly, H. J. Kollmeier, W. Lidy, H. Schator, and M. Wiemann, *J. Cell. Plast.*, **13**, 26 (1977).
4. G. Rossmly, W. Lidy, S. Schator, M. Wiemann, and H. J. Kollmeier, *J. Cell. Plast.*, **15**, 276 (1979).
5. G. Rossmly, H. J. Kollmeier, W. Lidy, H. Schator, and M. Wiemann, Cellular and Non-cellular Polyurethanes, Internal Conference, Urethane Division of the Society of Plastics Industry, Strasbourg, France, June 9-13, 1980, p. 635.
6. R. L. Rowton, *J. Cell. Plast.*, **16**, 287 (1980).
7. A. Lambert, *Eur. J. Cell. Plast.*, **3**(1), 25 (1980).
8. A. Van Thuyne and B. Zeegers, *J. Cell. Plast.*, **14**, 150 (1978).
9. R. Jennings, *J. Cell. Plast.*, **5**, 1 (1969).
10. L. H. Hanusa and R. N. Hunt, *J. Cell. Plast.*, **18**, 100 (1982).
11. F. E. Bailey and F. E. Critchfield, *J. Cell. Plast.*, **17**(6), 333 (1981).
12. S. D. Lipshitz and C. W. Macosko, *J. Appl. Polym. Sci.*, **21**, 2029 (1977).
13. J. H. Saunders and K. C. Frisch, *Polyurethanes, Chemistry and Technology*, Wiley-Interscience, New York, 1962, Part I, p. 145.

Received December 29, 1982

Accepted January 14, 1983