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THE DEGRADATION OF POLYURETHANE

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ABSTRACT

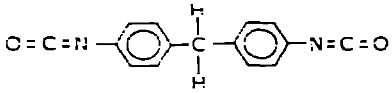
The aging of polyurethane was investigated by means of the isothermal storage test, adiabatic storage test and differential thermal analysis. Experiments were done between 318 and 493 K. Depending on temperature and degree of conversion, two successive reactions played a role in the aging process. For both reactions the apparent activation energy as well as the frequency factor could be determined. The apparent activation energy was about equal, but the frequency factor differed by a factor of 10^4. For low temperatures (below 373 K) only the first reaction is important. This reaction is strongly accelerated by oxygen and water vapour. By means of gas chromatography carbon dioxide could be detected as the gaseous product of "dry" aging, whereas carbon dioxide and hydrogen were the degradation products of "wet" aging. By means of thin layer chromatography and nuclear magnetic resonance it could be proved that "wet" aging was accompanied by hydrolysis.

INTRODUCTION

For many years, investigations have been performed concerning the compatibility of high energetic substances and construction materials (such as polymers, metals, etc.). Incompatibility can sometimes be caused by small amounts of degradation products from the construction material affecting the high energetic substance. Therefore, it seemed interesting to investigate the aging of polyurethane, which is frequently used in combination with high energetic substances. To meet the storage conditions common in practice, it was necessary to use a low temperature aging method that could be expected to give reliable results. The results were compared with those of a high temperature method.

MATERIALS

The polyurethane consisted of 71.4% (w/w) castor oil and 28.6% (w/w) Desmodur VL. Castor oil consists of a mixture of the glycolates of ricinoleic acid (8.0% w/w), stearic acid (0.3% w/w), oleic acid (8.0% w/w) and linoleic acid (3.6% w/w). Desmodur VL consists mainly of bis-(4-isocyanophenyl) methane (MDI)



and some homologues. Both Desmodur VL and castor oil were ordered from Bayer.

These two components of polyurethane were mixed in the above-mentioned ratio, after which polymerisation took place. Prior to testing, the polymer was ground as fine as possible.

EXPERIMENTAL

The degradation of polyurethane was studied using the isothermal storage test (IST) for low temperatures (i.e. temperatures between 318 and 383 K) [1] and isothermal differential thermal analysis (DTA) for high temperatures (i.e. temperatures between 405 and 493 K) [2] as well as the adiabatic storage test (AST) for intermediate temperatures (i.e. 391—413 K) [4].

The isothermal and adiabatic heat generation meters were constructed in the Prins Maurits Laboratory of TNO. The isothermal DTA experiments were carried out on a Mettler type TA-2000. A Becker Multigraph, type 409 gas chromatograph was used to study the gaseous degradation products of polyurethane. To study the fluid and solid degradation products, nuclear magnetic resonance (NMR) spectra were obtained from some aged and unaged samples of polyurethane, using a Varian XL-100.

MEASUREMENTS

The IST experiments

These experiments were performed in a stainless steel container of about 74×10^{-6} m^3. The container was closed with a stainless steel membrane, which breaks at about 5 bar overpressure. The heat generation was measured with respect to a reference container filled with 5 g of glass pearls [1]. The sample container was filled with 2.5 g of polyurethane. In imitation of Van

Geel [1], the degree of filling was expressed using the following equation

$$\epsilon_{O_2} = 0.2\left(\frac{\rho_g}{\rho_b} - 1\right) = 0.2\left(\frac{\rho_g}{M}\times V - 1\right) - V \qquad (1)$$

Knowing the sample weight (M), the volume of the container (V) and the density of polyurethane (ρ_g = 1130 kg m^{-3}), ϵ_{O_2} could be calculated, and amounted to 6.5.

In Fig. 1 the heat generation in the sample is logarithmically plotted as a function of the logarithm of time for the results of the IST experiments between 318 and 383 K as well as the isothermal DTA experiments between 405 and 493 K. Every experiment was performed in duplicate, while the mean values were calculated and worked out further. Differences between the duplicates were less than 10%.

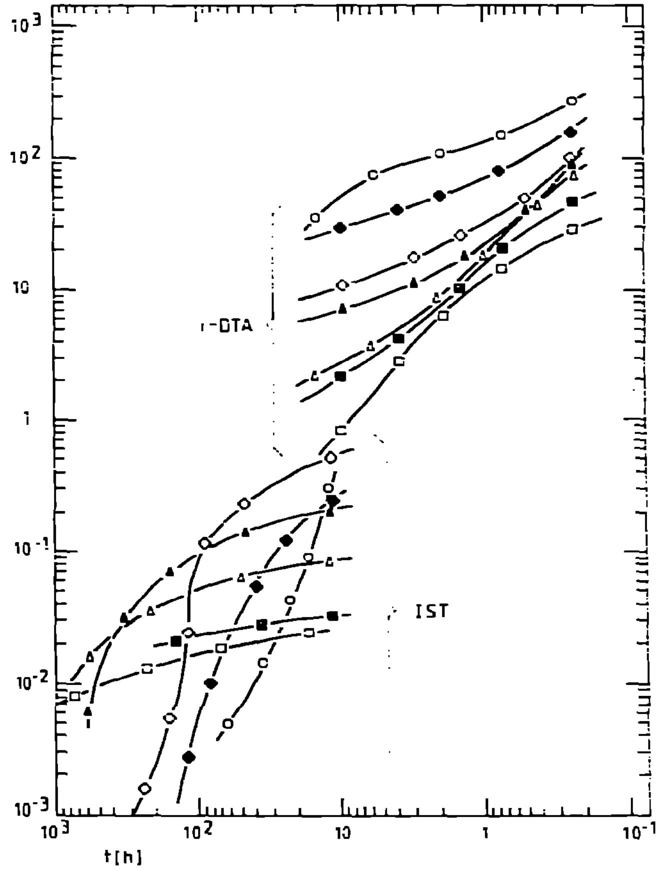


Fig. 1. Logarithmic plot of the heat generation (q) as a function of time (t) of the IST and isothermal DTA experiments at different temperatures.
IST (ϵ_{O_2} = 6.5): ○, 383 K; ◆, 368 K; ◇, 358 K; ▲, 348 K; △, 338 K; ■, 328 K; □, 318 K.
i-DTA (open containers): ○, 493 K; ◆, 473 K; ◇, 448 K; ▲, 435 K; △, 423 K; ■, 414 K; □, 405 K.

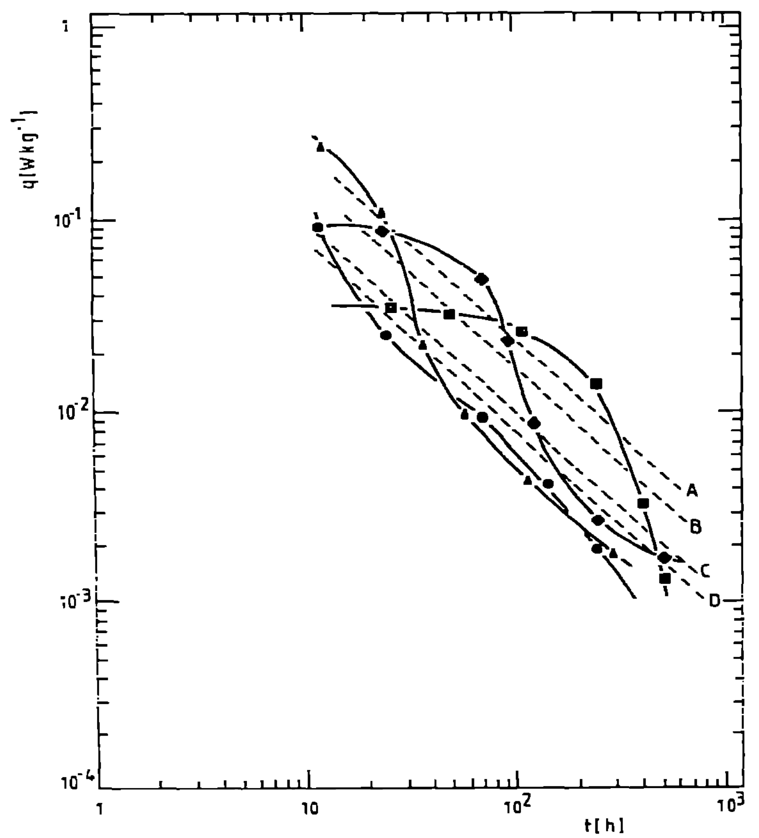


Fig. 2. Logarithmic plot of the heat generation (q) as a function of time (t) of four IST experiments at different temperatures with ϵ_{O_2} = 1.1. ●, 358 K; ▲, 348 K; ◆, 338 K; ■, 328 K.

To investigate the influence of the degree of filling, some experiments were performed with 12.5 g of polyurethane (ϵ_{O_2} = 1.1). The results of these experiments are plotted in Fig. 2 in the same way as in Fig. 1.

To check the influence of water, some experiments were performed with saturated water vapour. A small tray of water was placed in the container before closing it, so that only gaseous contact was possible. The results are presented and compared with dry experiments in Fig. 3.

The isothermal DTA experiments

The isothermal DTA experiments [2] were performed in duplicate at temperatures between 405 and 493 K. Use was made of open stainless steel holders of 0.5×10^{-6} m^3. In every experiment a sample of about 80 mg was used. In accordance with Borchardt and Daniels [3], the DTA output signal was translated into a heat generation. As with the IST experiments, the mean values were calculated (see Fig. 1). Differences between duplicates were less than 10%.

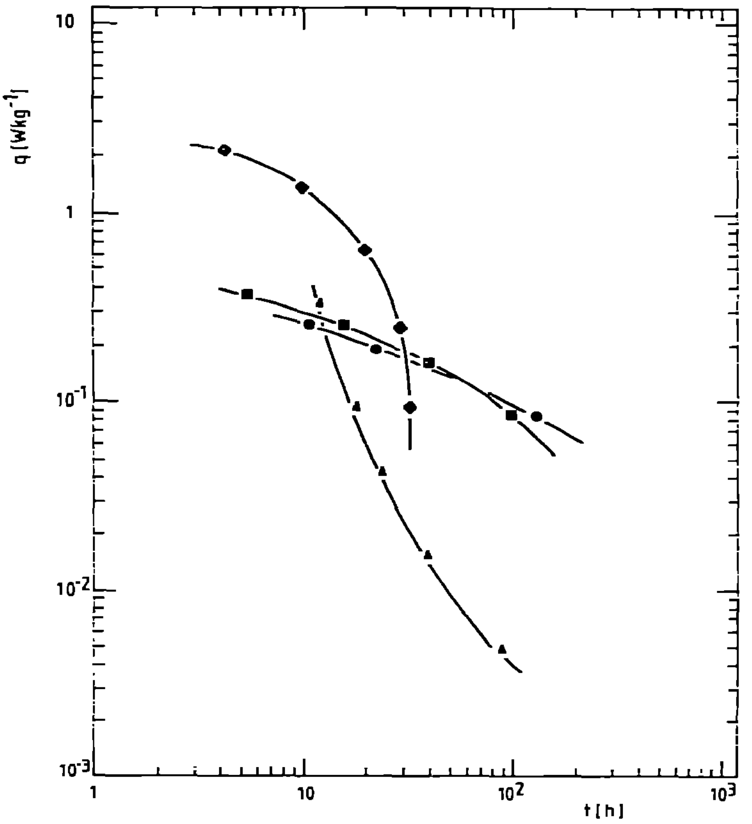


Fig. 3. Logarithmic plot of the heat generation (q) as a function of time (t) of four IST experiments with ϵ_{O_2} = 6.5. ◆, 368 K under moist air; ▲, 383 K under dry air; ■, 348 K under moist air, ●, 348 K under dry air.

The AST experiments

The AST experiments were performed with 0.24 kg of polyurethane in a closed vessel of about 10^{-3} m^3, which was purged with air. With AST experiments a sample is heated until the heat generation exceeds the heat losses and the sample starts heating itself [4]. With polyurethane this took place at 391 K. The experiment was stopped at 413 K and, after cooling, repeated. In this way some successive experiments with the same sample were performed. During every experiment the degree of conversion was assumed to be constant. This assumption is acceptable because of the difference between the heat generated in one AST experiment and the reaction enthalpy.

Gas analyses

For the gas chromatographic investigation of the gaseous products of polyurethane aging, use was made of two different columns.

(1) a column filled with poropak QS, in combination with a helium flow

(17×10^{-6} m^3 s^{-1}) as a carrier gas, an oven temperature of 303 K and a wire-type katharometer to measure carbon dioxide;

(2) a column, filled with molecular sieve 5A, in combination with an argon flow (17×10^{-6} m^3 s^{-1}) as carrier gas, an oven temperature of 303 K and a wire-type katharometer to measure hydrogen.

Gaseous products of dry and wet aging in conformity with the IST conditions at 358 and 368 K were investigated. The only detectable gases were carbon dioxide and hydrogen.

Nuclear magnetic resonance (NMR)

The separation of the non-gaseous aging products of polyurethane was carried out using a method according to Dawson et al. [5]. Following this method polyurethane is hydrolysed and separated by means of extraction of the aqueous phase with ether several times. This eventually yields an ether extract and an aqueous layer, which may be investigated separately. This procedure was applied for Desmodur VL and unaged polyurethane. In the aqueous layer no products could be detected, but in the ether extract different products could be further separated by means of thin layer chromatography (TLC), with silica gel as carrier material and a mixture of 1,2-dichloroethane and ethylacetate (21 : 1) as mobile phase. This procedure, with and without alkaline hydrolyses, was also applied for aged polyurethane. The clearest spots on the TLC material were used for a 100 MHz NMR analysis in deuterated chloroform as solvent with tetramethylsilane as reference.

RESULTS AND DISCUSSION

From curves of the logarithmic heat generation as a function of the total heat, the points of isoconversion could be determined at every temperature and degree of conversion. This procedure was followed for both the IST and isothermal DTA experiments (see Figs. 4 and 5).

For aging processes the following equation is valid [1]

$$q_t = \mathrm{F}(Q) \exp\left(-\frac{E}{RT}\right) \qquad (2)$$

Since F(Q) is a function of the degree of conversion only, eqn. (2) may be transformed into

$$\log q_t = \log \mathrm{F}(Q) - \frac{E}{2.303\, RT} \qquad (3)$$

So, from the slope of the lines representing the logarithmic heat generation as a function of the reciprocal temperature, the apparent activation energy of the process could be calculated. The intercept of the ordinate may be used to calculate F(Q) (the heat generation factor).

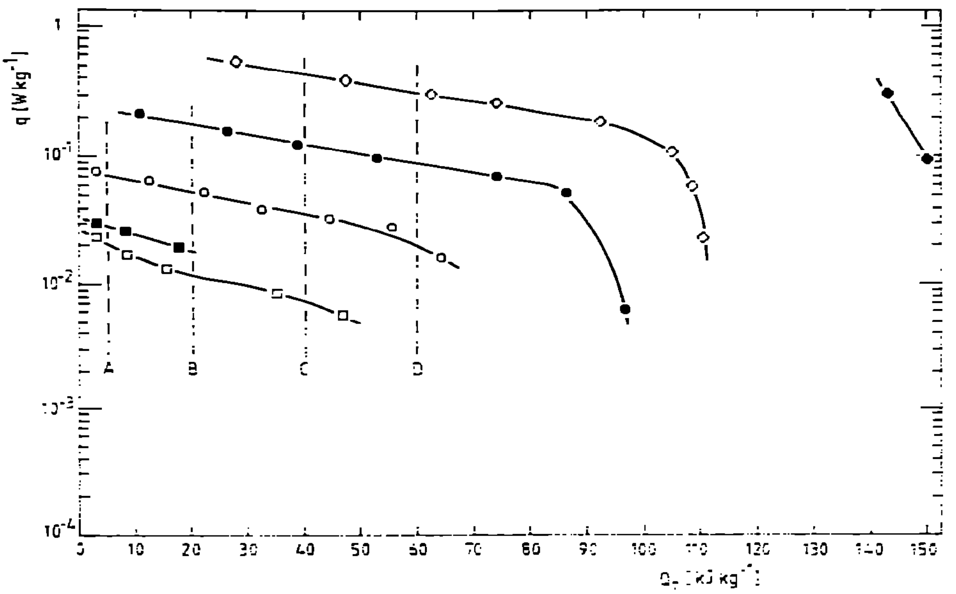


Fig. 4. Semi-logarithmic plot of the heat generation (q) as a function of the total heat (Q_t) of the IST experiments with ϵ_{O_2} = 6.5 at different temperatures. ◆, 383 K; ◇, 358 K; ●, 348 K; ○, 338 K; ■, 328 K; □, 318 K.

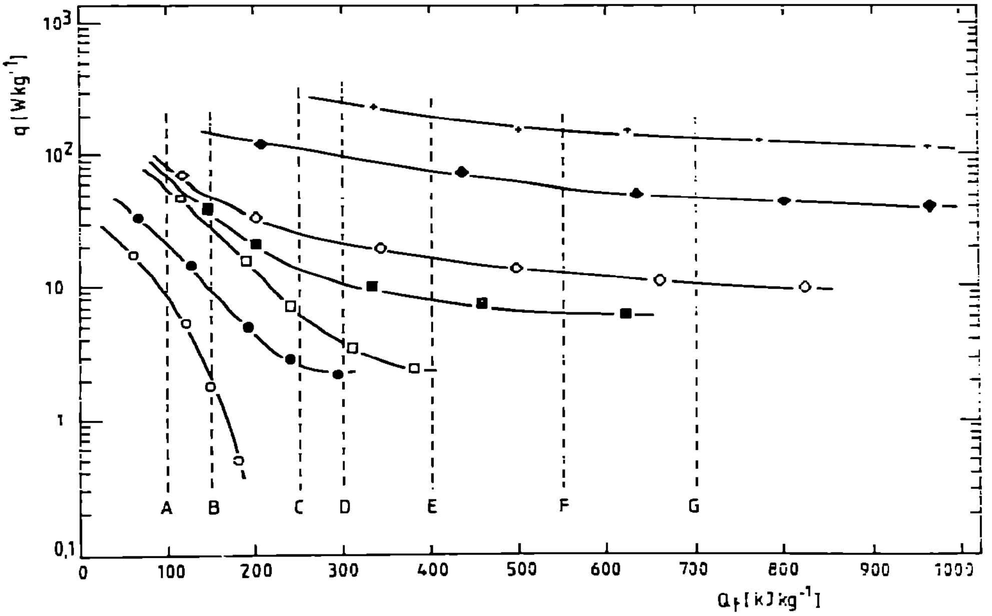


Fig. 5. Semi-logarithmic plot of the heat generation (q) as a function of the total heat (Q_t) of the isothermal DTA experiments with open containers, at different temperatures. +, 493 K; ◆, 473 K; ◇, 448 K; ■, 435 K; □, 423 K; ●, 414 K; ○, 405 K.

TABLE I

Values of the apparent activation energy and heat generation factor for the aging of polyurethane at different temperatures and Q_t values

Method of measuring	Open or closed vessel	Mass of solid involved (g)	c_{O_2} (see text)	Temperatures involved (K)	Heat evolved (Q_t) (kJ kg^{-1})	Apparent activation energies (kJ mole^{-1})		Heat generation factors (W kg^{-1})		
						E	SD[a]	F(Q)	Min.[b]	Max.[b]
IST	Closed	12.5	1.1	328–358	A Rising	117	2	3.0×10^{19}	1.2×10^{19}	7.8×10^{9}
					B (see	115	1.5	10×10^{18}	6.5×10^{18}	17×10^{18}
					C Fig. 3)	117	2	10×10^{18}	5.1×10^{18}	20×10^{18}
					D	114	8.5	22×10^{17}	1.2×10^{17}	420×10^{17}
IST	Closed	2.5	6.5	328–358	B 20 (see	106	2	15×10^{17}	7.5×10^{17}	29×10^{17}
					C 40 Fig.2)	121	6.5	18×10^{19}	2.1×10^{19}	160×10^{19}
					D 60	136	1	1.9×10^{22}	1.4×10^{22}	2.6×10^{22}
AST	Closed and purged with air	240	—	391–413	185– 251	125	5.5	6.0×10^{15}	1.6×10^{15}	29×10^{15}
					345– 405	112	2	19×10^{14}	1.8×10^{14}	53×10^{14}
					484– 561	117	4	3.9×10^{14}	1.3×10^{14}	12×10^{14}
					638– 703	100	2.5	2.6×10^{12}	1.3×10^{12}	5.3×10^{12}
					799– 878	102	1	4.7×10^{12}	3.6×10^{12}	6.5×10^{12}
					990–1068	106	2	13×10^{12}	7.2×10^{12}	24×10^{12}
					1150–1229	108	3	20×10^{12}	7.9×10^{12}	48×10^{12}
					1316–1394	108	2	18×10^{12}	9.7×10^{12}	32×10^{12}
					1473–1538	106	3.5	10×10^{12}	1.9×10^{12}	48×10^{12}
					1614–1675	106	6	10×10^{12}	1.8×10^{12}	53×10^{12}
					1749–1814	106	2	4.0×10^{12}	4.8×10^{12}	16×10^{12}
Isothermal DTA	Open	80×10^{-3}	—	414–493	C 250 (see	98	4.5	7.3×10^{12}	2.3×10^{12}	23×10^{12}
					D 300 Fig. 5)	103	4.5	24×10^{12}	7.8×10^{12}	71×10^{12}
					E 400	99	3.5	6.7×10^{12}	2.9×10^{12}	16×10^{12}
					F 550	98	3.5	3.9×10^{12}	1.6×10^{12}	10×10^{12}
					G 700	106	1.5	2.3×10^{13}	1.7×10^{13}	3.1×10^{13}

[a] SD = standard deviation.

[b] Min. and max. on the basis of the standard deviation.

From the IST experiments with $\epsilon_{O_2} = 1.1$ the isoconversion points were obtained by drawing straight lines with a slope of 45° (the so-called isoconversion lines) in the logarithmic heat generation—time diagram (see Fig. 2).

With the AST experiments the heat generation can be drawn directly as a function of the reciprocal temperature to calculate the apparent activation energy and heat generation factor. These calculations were performed by computer using the least squares method. The results are presented in Table 1.

From Table 1 it is clear that with increasing degree of conversion, at low temperatures (IST experiments with $\epsilon_{O_2} = 6.5$) both the apparent activation energy (higher energy barrier) and the heat generation factor (reaction more probable) increase. At higher degree of filling ($\epsilon_{O_2} = 1.1$) the apparent activation energy and heat generation factor remain constant, but with these experiments there is hardly any increase in the degree of conversion.

At higher temperatures (isothermal DTA experiments) the apparent activation energy and heat generation factor are lower. Below $Q_t = 250$ kJ kg^{-1} no calculations could be made, because the curves show a change in mechanism or reaction in that region. This is well illustrated in Fig. 5 by the deviating course of the two upper curves as compared with the other curves. From Fig. 5 it appears that this change takes place at about 423 K when a quantity of heat of about 250 kJ kg^{-1} has been generated. This agrees with a non-isothermal DTA curve of polyurethane (not shown) — low heating rate — which has a maximum at 423 and 523 K.

One would expect this change in reaction to occur at every aging temperature. However, this does not appear from the curves of Fig. 5, because in this series of experiments at the highest temperatures (above 448 K) this change took place before the first measuring point, and at lower temperatures (405 K) the experiment was stopped before the change could take place; so, at these temperatures the change remained unnoticed. The assumption is confirmed by the AST experiments. They show that up to $Q_t = 600$ kJ kg^{-1} the apparent activation energy and heat generation factor agree with values from the IST experiments. At higher Q_t values the agreement of the results of the AST experiments with those of the isothermal DTA experiments is better.

To obtain more general kinetic data of the degradation process, this was assumed to be a homogeneous reaction. This is usually the case for polymer degradations [2]; so, the following equation is valid

$$-\frac{\mathrm{d}m_t}{\mathrm{d}t} = km_t^n \qquad (4)$$

In this equation m_t is the amount of active groups still present at time t. If x is the degree of conversion and m_0 the amount of reactive groups originally present, eqn. (4) may be transformed into

$$\frac{\mathrm{d}x_t}{\mathrm{d}t} = km_0^{n-1}(1-x_t)^n \qquad (5)$$

When the reaction mechanism does not change, the following equation is valid

$$x_t = \frac{Q_t}{Q_0} \tag{6}$$

So eqn. (5) becomes

$$\frac{dQ_t}{dt} = q_t = km_0^{n-1}\left(1 - \frac{Q_t}{Q_0}\right)^n Q_0 \tag{7}$$

or

$$\log q_t = \log(km_0^{n-1}Q_0) + n \log\left(1 - \frac{Q_t}{Q_0}\right) \tag{8}$$

where k = rate constant; q_t = heat generation at time t; n = reaction order; Q_0 = reaction enthalpy; Q_t = total heat, generated until time t.

With small conversions the following approximation may be made

$$-\ln(1 - x_t) = x_t \tag{9}$$

This leads to

$$\log q_t = \log(km_0^{n-1}Q_0) - \frac{n}{2.303\, Q_0} \times Q_t$$

or

$$\log q_t = \log(k'Q_0) - \frac{n}{2.303\, Q_0} \times Q_t \tag{10}$$

Using eqn. (10), n and k' may be evaluated from Figs. 4 and 5 by measuring the slope of the straight parts and extrapolating to $Q_t = 0$. The reaction enthalpy was estimated by long-term isothermal DTA experiments at 423 and 523 K and amounted to 670 and 12 000 kJ kg^{-1} respectively. For the IST experiments, Q_0 = 670 kJ kg^{-1} was used in eqn. (10). For the isothermal DTA experiments, Q_0 = 670 and 12 000 kJ kg^{-1} were used. With the successive AST experiments the same procedure could be used by looking for the corresponding Q_t and q values of the same temperature and using Q_0 = 12 000 kJ kg^{-1}. By using eqn. (10) the errors never exceed 8—9%.

The results are collected in Table 2. In Fig. 6 the values of Table 2 have been calculated in two Arrhenius plots. It appears that the experiment at 435 K (curve 12 in Fig. 5) does not agree with both reaction courses (see points A and B in Fig. 6). Probably the two reactions are interfering with each other at that temperature within the range of Q_t values.

From the two Arrhenius plots the apparent activation energy (E) could be calculated from the slope and the frequency factor (k_0) from the intercept. The results were:

TABLE 2

Values of n and k' for the aging of polyurethane at different temperatures and Q_t values

Method of measuring	Temp. (T) (K)	Reciprocal temp. ($1/T$) (10^{-3} k^{-1})	Reaction enthalpy (kJ kg^{-1})	Traject of Q_t used (kJ kg^{-1})	Order of reaction		Rate constant (s^{-1})	
					n	SD [a]	k'	SD [a]
IST	328	3.05	670	Whole curve	22	2	5.2×10^{-8}	0.2×10^{-8}
	338	2.96		< 60 (see	13.8	0.5	12.5×10^{-8}	0.3×10^{-8}
	348	2.87		< 90 Fig. 4)	11.9	0.3	38×10^{-8}	1×10^{-8}
	358	2.79		<100	10.9	0.2	123×10^{-8}	3×10^{-8}
AST	397	2.52	12 000	>600	4.7	0.7	1.7×10^{-8}	0.15×10^{-8}
	400	2.50		>600	4.2	0.5	2.0×10^{-8}	0.1×10^{-8}
	403	2.48		>500	4.5	0.3	2.78×10^{-8}	0.07×10^{-8}
	406	2.46		>500	4.0	0.2	3.30×10^{-8}	0.06×10^{-8}
	410	2.44		>500	6	1	5.4×10^{-8}	0.6×10^{-8}
Isothermal DTA	405	2.47	670	<110 (see	11.5	0.15	6.8×10^{-5}	0.1×10^{-5}
	414	2.42		<220 Fig. 5)	9.9	0.2	13.2×10^{-5}	0.4×10^{-5}
	423	2.36		<220	9.4	0.5	33×10^{-5}	4×10^{-5}
	435	2.30		<220	8.3	0.2	36×10^{-5}	2×10^{-5}
	435	2.30	12 000	>450 (see	61	4	10.3×10^{-8}	0.4×10^{-8}
	448	2.23		>450 Fig. 5)	15	1.5	88×10^{-8}	6×10^{-8}
	473	2.11		>500	5.7	0.4	240×10^{-8}	10×10^{-8}
	493	2.03		>500	5.0	0.15	640×10^{-8}	15×10^{-8}

[a] SD = standard deviation.

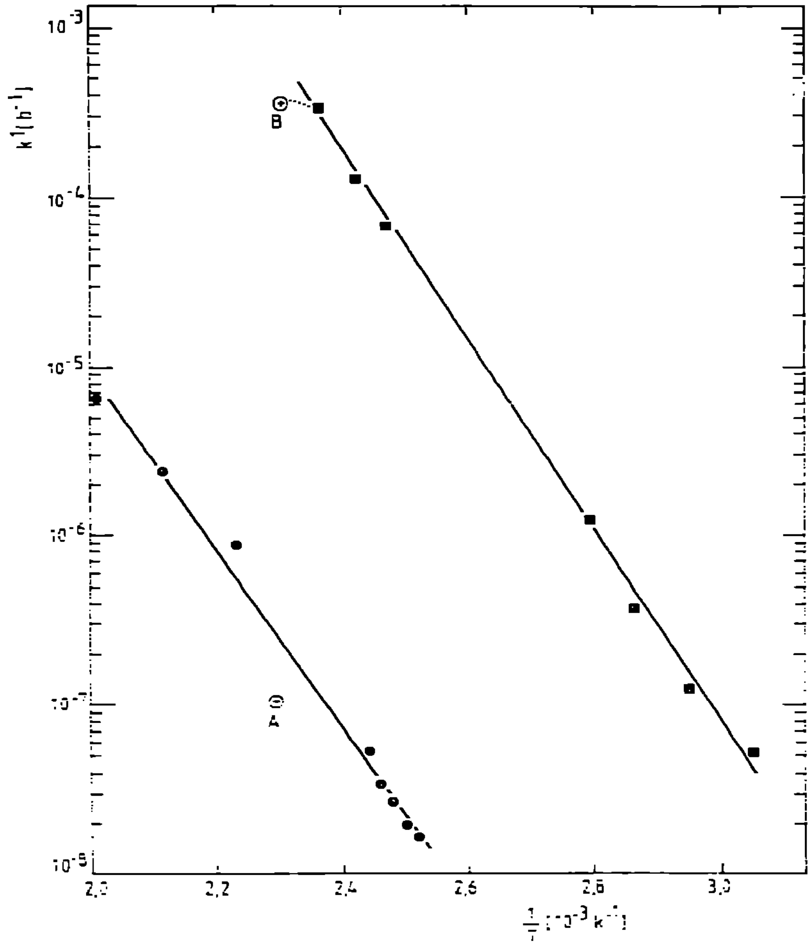


Fig. 6. Arrhenius plots of the two reaction courses of the degradation of PU. ■, Determined from the IST and i-DTA experiments; ●, determined from the AST and i-DTA experiments (points A and B refer to the i-DTA experiment at 435 K, which was determined with Q_0 = 670 and 12 000 kJ kg^{-1}, respectively).

curve 1 (IST and isothermal DTA experiments):

E = 106 kJ mole^{-1}	SD = 1.5 kJ mole^{-1}
$k_0 = 3.7 \times 10^9$ s^{-1}	$2.3 \times 10^9 < k_0 < 6.0 \times 10^9$

curve 2 (AST and isothermal DTA experiments):

E = 102 kJ mole^{-1}	SD = 3 kJ mole^{-1}
$k_0 = 5.0 \times 10^5$ s^{-1}	$2.1 \times 10^5 < k_0 < 11 \times 10^5$

These results show that there is a small overlap in apparent activation energies of the two reactions, but for the rest they confirm the former conclusion, that there are two degradation processes. The first process has a somewhat higher apparent activation energy than the second, but is more probable. For storage problems at low temperatures (below 373 K) it seems logical that only the first process will be important.

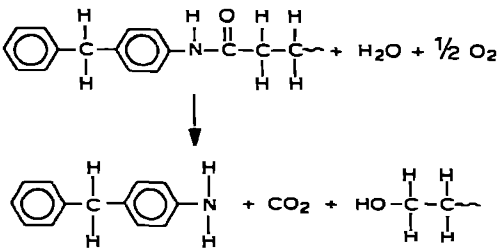
From Fig. 2 it appears that at higher degrees of filling the heat generation suddenly collapses. This is probably due to a lack of oxygen in the container if more sample is present. Experiments under an atmosphere of nitrogen showed that the total area under the curve was less than 10% compared with the corresponding experiment under air. Apparently oxygen is important in the degradation process of polyurethane.

Figure 3 shows that humidity may also be important. It appears that at 368 K the heat flow is much higher when water vapour is present than in the corresponding dry experiment, while at 348 K there is hardly any difference. The wet reaction at 368 K then suddenly collapses and becomes endothermic (not drawn). The endothermicity of the process is more or less confirmed by the gas chromatographic investigations of the aging products, because hydrogen was present after 2 weeks of "wet" aging at 368 K, unlike with "dry" aging. The evolution of carbon dioxide is higher with the "wet" experiments than with the corresponding "dry" experiments. With aging at 358 K there is no difference in gaseous products between "dry" and "wet" aging.

With "wet" aging there are probably two degradation processes, the usual process of "dry" aging and some cracking. The usual process will be faster under "wet" conditions — high heat generation (see Fig. 3) and much carbon dioxide — and soon come to an end, after which the cracking process — endothermic with hydrogen evolution — will start. This is confirmed by the fact that after 1 week of "wet" aging no hydrogen could be detected and the polyurethane appeared unchanged, as with "dry" aging. However, after 2 weeks of "wet" aging, hydrogen could be detected in the gaseous phase, while the polyurethane had become a viscous product. This viscous product could be investigated by means of TLC and NMR. The spots on the thin layer chromatogram were compared with those of unaged polyurethane. In one case the NMR spectra of the extracts of the spots show a remarkable resemblance. These spectra appeared to belong to MDI, the main component of Desmodur VL. This was confirmed by two peaks at 24.0×10^{-10} m and 28.8×10^{-10} m in the UV spectrum [6]. No more spots could be cleared up in this way.

The presence of MDI in the reaction mixture points to depolymerisation accompanying "wet" aging. This would also confirm the observed endothermic effects. Attempts to investigate the non-gaseous products of "dry" aging in this way also failed, because they could not be dissolved without alkaline hydrolysis.

According to literature [7,8] it is acceptable that in the presence of a wet atmosphere at 368 K the urethane bonding is hydrolysed in the following way:



A pure thermal degradation in this way is unlikely to occur at lower temperatures [9—11]. This makes it difficult to explain the exothermic effects found with "dry" aging. A real possibility would be that the polymerisation was not completed during the preparation of polyurethane and that this process was continuing during the thermal experiments. But this does not explain the evolution of carbon dioxide and the influence of oxygen on the course of the IST experiments. Another possibility is that some decomposition of ester bondings with poor hydrolytic stability takes place, followed by decarbonification of the resulting acid functions [12]. This may have also happened with the "dry" experiments, because water was not totally excluded. However, such decomposition processes would be endothermic instead of exothermic. Another mystery is the question of how hydrogen can evolve at such low temperatures. To resolve all these effects, more investigations on the substance itself will be necessary besides the thermal experiments.

CONCLUSIONS

(1) The aging of polyurethane is caused by two successive processes. From both processes the kinetic parameters can be determined. The two processes have approximately the same energy barrier, but the first process is much more probable than the second. Therefore, at low temperature aging only the first process has to be considered.

(2) Oxygen as well as water vapour seem to promote the aging process. Water vapour, especially, has a devastating influence on polyurethane at temperatures above 368 K.

(3) The mechanism of the aging processes is unknown. To resolve this, more investigations on the substance itself are necessary.

REFERENCES

1 J.L.C. Van Geel, Thesis, Delft University of Technology, 1969.
2 J. Šesták, V. Satava and W.W. Wendlandt, Thermochim. Acta, 7 (1973) 333.
3 H.J. Borchardt and F. Daniels, J. Am. Chem. Soc., 79 (1957) 41.
4 H.J. Pasman, Th.H. Groothuizen and C.H. Vermeulen, Explosivstoffe, 7 (1969) 151.

5 B. Dawson, S. Hopkins and P.R. Sewell, J. Appl. Polym. Sci., 14 (1970) 35.
6 H.A. Szymanski, A. Bluenke and W. Collins, Appl. Spectrosc., 19 (1965) 137.
7 A.G. Dement'ev, L.V. Nevskii and I.I. Mikheeva, Int. Polym. Sci. Technol., 2 (1975) T/99.
8 M.L. Matuszak, K.C. Frisch and S.L. Reegen, J. Polym. Sci., Polym. Chem. Ed., 11 (1973) 1683.
9 M.L. Matuszak and K.C. Frisch, J. Polym. Sci., Polym. Chem. Ed., 11 (1973) 637.
10 W.D. Wooley, J. Fire Flame Combust. Toxicol., 1 (1974) 259.
11 F.D. Hilleman, K.J. Voorhees, L.M. Wojcik, M.M. Birly, P.W. Ryan and I.N. Einhorn, J. Polym. Sci., Polym. Chem. Ed., 13 (1975) 571.
12 L.A. Wall and J.H. Flynn, Rubber Chem. Technol., 35 (1962) 1157.