Internal Heat Generation and Fatigue Life Behaviour of Polyurethane Elastomer Based on Trans 1, 4 - Cyclohexane Diisocyanate

Key Words:

polyurethane, urethane elastomer, heat generation, fatigue life, excess diisocyanate

M. Barikani* and C. Hepburn

Loughborough University of Technology, Loughborough, Leicestershire, LE11, 3TU, U. K

ABSTRACT

Internal heat generation of castable polyester polyurethane elastomers based on the system polycaprolactone diol(Capa 225)/trans 1,4-cyclohexane diisocyanate(CHDI)/1,4-butane diol(1,4-BD) and 1,4-cyclohexane dimethanol(1,4-CHDM)was measured on the De mattia-machine by using a contact flat thermocouple head during the flex cracking resistance measurements. It was found that the heat generation of these polymers increased with excess percentages of diisocyanate and applied strain. It was also found that both crack initiaion and crack propagaion resistance decreased with increasing crosslinking due to the excess diisocyanate.

INTRODUCTION

The effect of various individual diisocyanate [1], mixture of diisocyanates in different polyol/ diisocyanate block ratios [2], and using excess CHDI on the thermal stability of polyurethane elastomers [3] were previously reported based on the linear polyol polycaprolactone (Capa 225). The relative thermal stability of these elastomers was enhanced considerably by using 1, 4 – cyclohexane diisocyanate and excess diisocyanate in polyurethane formulations. In this paper, the internal heat generation and fatigue life behaviour of CHDI based polyurethane were studied. Using excess diisocyanate, the relationships between excess CHDI and fatigue life are discussed according to their flex cracking and cut growth properties.

EXPERIMENTAL

The materials used in this study are listed in Table 1.

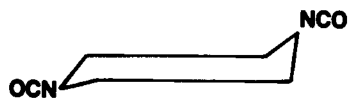
Both polyol and chain extenders were dried and degassed at 100°C under vacuum for at least 1h before use. All polyurethanes were prepared by the method described in our previous papers [1 – 3]. The molar ratio of polyester diol (Capa 225), CHDI, and 1, 4 – BD + 1, 4 – CHDM was 1:3:2.

Polymer Characterization

Fatigue life of some of the prepared polyurethanes was determined on a De Mattia – type machine* (See Figure 1) for resistance to flex cracking and cut growth by using a special test specimen. The test piece, which was a rectangular strip of approximate dimensions 100 mm × 10 mm × 2 mm, was die cut from the cast sheet and it was fixed in two clamps which moved towards each other to extend and bend the strip. Repeated extending, bending, or flexing caused cracks to develop in bending part of the surface. Where tension strains or stresses were set up during flexing, the bending part of the surface contained a crack or cut causing it to extend in a direction perpendicular to the strain or stress. The apparatus was operated at 300 cycles/minute and the tests were continued until the complete failure of the test pieces occurred; then the number of cycles were recorded. The tests were made at a number of extensions for crack propagation, and the compounds were compared in the terms of fatigue life at the same strain.

* Present address: Polymer Research Center of Iran, P.O.Box 14185/458, Tehran, Iran.

Table 1: Materials used in these polyurethane formulations

materials	Abbreviation	Chemical formula	Molecular weight	Suppliers
Polyesterdiol Polycaprolactone	CAPA 225	$HO-[(CH_2)_5-\overset{O}{\overset{\Vert}{C}}-O]-CH_2CH_2-[O-\overset{O}{\overset{\Vert}{C}}-(CH_2)_5]_n-OH$	2000	Laporte* Industries, Interox Chemicals Ltd. Luton. UK
Diisocyanate Trans – 1, 4 cyclohexane diisocyanate	CHDI Elate 166		166	Armak Co. Chicago. USA
Chain extenders 1, 4 – Butanediol	1. 4 – BDO	$HO-CH_2-CH_2-CH_2-CH_2-OH$	90	GAF (Great Britain) Co. Ltd, Manchester,/UK
1, 4 Cyclohexane dimethanol	1, 4 – CHDM	$HOCH_2-CH<(CH_2-CH_2)(CH_2-CH_2)>CH-CH_2OH$	144.21	Aldrich Chemical Co. Gillingham. Dorset, UK
Catalyst Dicarbobutyloxy ethyl tin dichloride	T220	$CH_3(CH_2)_3-O-\overset{O}{\overset{\Vert}{C}}-(CH_2)_2$, $CH_2(CH_2)_2-O-\underset{O}{\underset{\Vert}{C}}-(CH_2)_2$ $>Sn<$ Cl, Cl		AkzoChemieBV,Amersfoort, The Netherlands

Initial cracks in the test piece were produced by piercing a 2mm long cut at a mid-point perpendicular to the longest side and equidistant from the sides, using a suitable cutter and jig. The cut was accomplished by a single insertion and withdrawal of the tool.

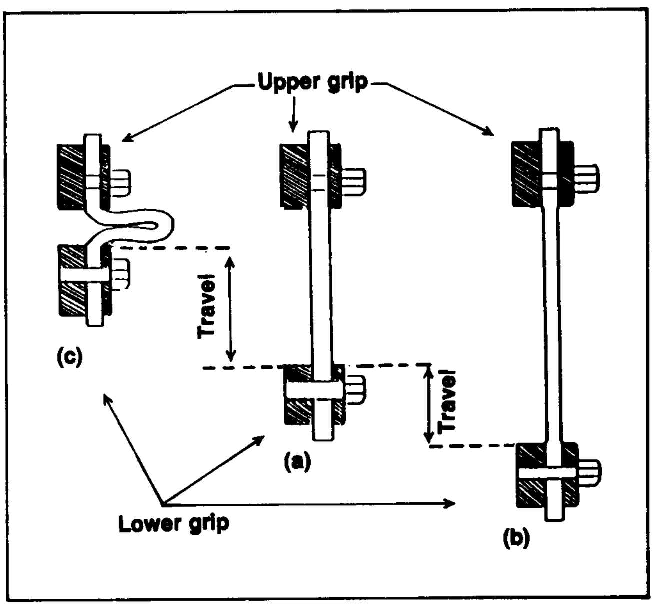


Figure 1: De Mattia – Type Machine:

a) Sample shown in its original form unstressed b) Sample under strain

c) Sample under stress

RESULTS AND DISCUSSION

Flex Cracking and Crack Growth

The results of the crack initiation and crack propagation tests by the De mattia machine are given in Tables 2 and 3. The results show the flex cracking resistance of polyurethane elastomers based on the Capa 225/CHDI/1, 4 – BD + 1, 4 – CHDM system decreases with increasing excess percent of CHDI. This was thought to be due to the higher modulus and lower extension at break ability of the more highly crosslinked polyurethanes, which resulted from the use of excess diisocyanate. A similar trend of decreasing fatigue life was also observed in the crack propagation test series, therefore both crack initiation and crack propagation resistance decreased with increasing crosslinking which were believed to be due to the use of the excess diisocyanate.

Figure 2 shows the relationship between fatigue life and excess percentage CHDI, and percentage applied strain of PU elastomers for both flex cracking and cut growth tests. It was found through Figure 2 (c) that the relationship between fatigue life and applied strain was similar to the «Wohler curve». The important feature of this curve was that reducing the stress or strain toward a particular value caused the fatigue life to increase virtually to infinity giving rise to the concept of a limiting fatigue life, and an ultimate failure strength or deformability.

* H. W. Wallace and Co. Ltd., Croydon, England.

Internal Heat Generation

The internal heat generation of the Capa 225/CHDI/ 1, 4 – BD + 1, 4 – CHDM based polyurethane elastomer was measured on the De Mattia – type machine by using a contact flat thermocouple head during the flex cracking resistance measurements. Temperature was recorded by a Comarck electric thermometer at time intervals which varied on the rate of temperature rise. The results are given in Tables 4 and 5 and Figures 3 and 4. Table 4 shows the results of heat generation of polymers subjected to 100% applied strain, and Table 5 gives the results at 150% applied strain.

Figures 3 and 4 show the effect of using various levels of excess diisocyanate and the percentage applied strain on heat generation of these PU elastomers. It is seen that the heat generation of these polymers increased with both increasing excess percentage diisocyanate and the percentage applied strain e.g., the increase in temperature for a polymer with 0.2% excess CHDI at 100% strain was 20°C and this increased to 29°C for a 30% excess CHDI containing polymer. The increase in temperature for the polymer containing 30% excess CHDI was about 29°C at 100% applied strain and this increased to about 37°C at 150% applied strain. Figures 3 and 4 also show that the temperature of polymers sharply increased during the first five minutes of flexing and then remained approximately constant as flexing time continued.

Table 2: Flex cracking resistance of polyurethane elastomer based on Capa 225 / CHDI 1,4 - BD + 1,4 - CHDM with molar ratio of 1/3/2 at 100% strain

Sample No	% Excess CHDI	Kilocycles to Failure at 100% Strain
Capa 18, 6	0.2	365
B 74	5	340
B 77	20	200
B 81	40	30

Table 3: Crack propagation resistance of polyurethane elastomer based on Capa 225/CHDI/1, 4 - BD + 1, 4 - CHDM with molar ratio of 1/3/2 at 0%, 10%, 20% and 25% strain

Sample No	% Excess CHDI	Number of Kilocycles to Failure			
		0%Strain*	10%Strain	20%Strain	25%Strain
Capa 18, 6	0.2	1000 (no failure)	1515 (no failure)	210	1. 1
B 74	5	1000 (no failure)	1515 (failed)	132	0.88
B 77	20	1000 No failure)	1070 (failed)	-	0.5
B 79	30	1000 (no failure)	72 (failed)	3.6	0.2
B 81	40	1000 (no failure)	13.4 (failed)	1.8	0.05

* At 0% strain the test was stopped after 1000 kilocycles.

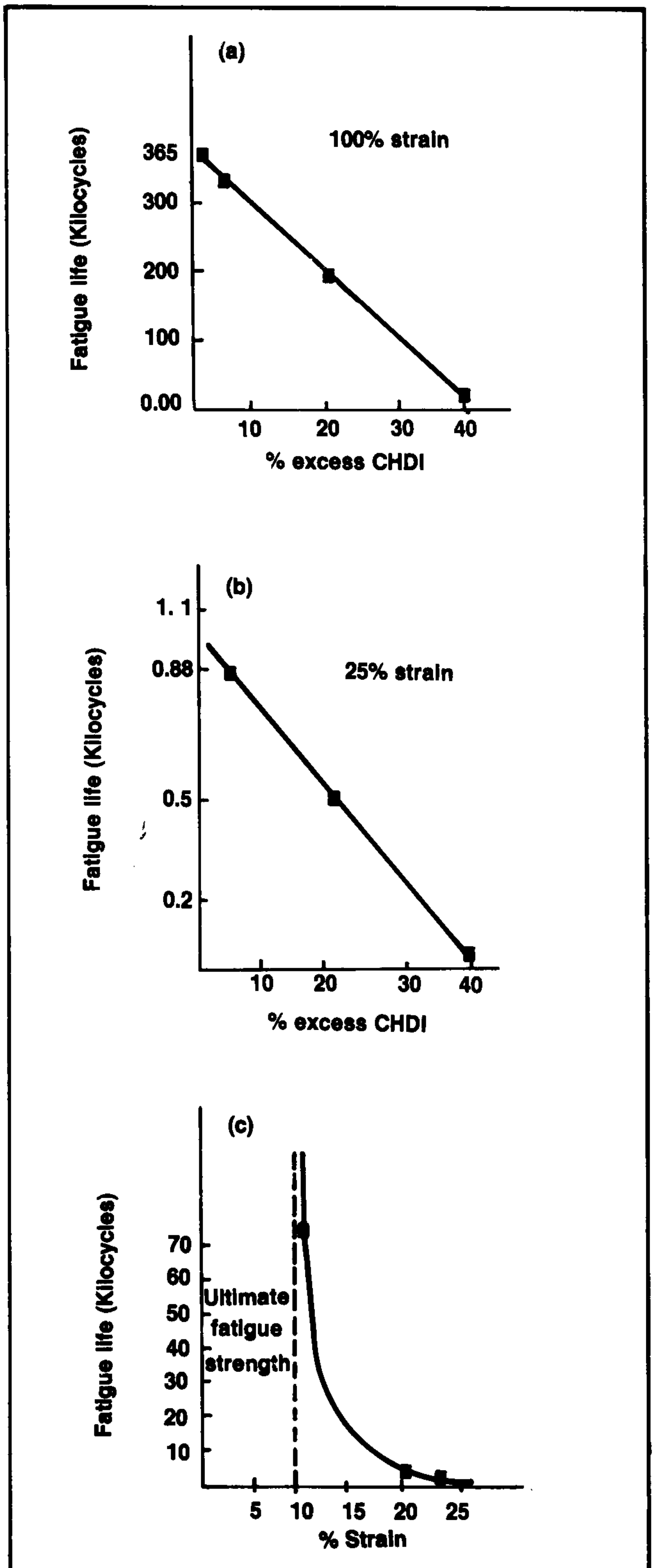


Figure 2: Relationship between fatigue life and % excess diisocyanate and also % applied strain of a polyurethane elastomer based on Capa 225/CHDI/1, 4 - BD + 1, 4 CHDM.
(a) Crack initiation; (b) and (c) Crack propagation

CONCLUSION

The effect of using excess CHDI on the internal heat generation and fatigue life of Capa 225/CHDI / 1, 4 - BD + 1, 4 - CHDM based polyurethane elastomers has been studied.

***Table 4:** Heat generation observed by flexing of polyurethane elastomers based on Capa 225 / CHDI / 1, 4 – BD + 1, 4 – CHDM at 100% strain*

$t_0 = 21^{\circ}C$

Time (mins)	Capa 18, 6 (0.2% excess CHDI)		B74 (5% excess CHDI)		B79 (30% excess CHDI)	
	t	Δt	t	Δt	t	Δt
1	34	13	37	16	41	20
2	38	17	38	17	46	25
3	39	18	42	21	47	26
6	40	19	43	22	47	26
10	40	19	43	22	48	27
20	40	19	44	23	49	28
30	41	20	44	23	50	29
45	41	20	44	23	50	29
60	41	20	44	23	50	29
90	41	20	44	23	50	29

***Table 5:** Heat generation observed by flexing of polyurethane elastomers based on Capa 225/CHDI / 1, 4 – BD + 1, 4 – CHDM at 15% strain*

$t_0 = 21^{\circ}C$

Time (mins)	B74 (5% excess CHDI)		B77 (20% excess CHDI)		B79 (30% excess CHDI)	
	t	Δt	t	Δt	t	Δt
1	40	19	45	24	48	27
2	44	23	48	27	54	33
3	44.5	23.5	48	27	55	34
4	45	24	49	28	56	35
10	47	26	50	29	57	36
15	47	26	50	29	58	37
20	47	26	50	29	58	37
30	48	27	50	29	58	37
65	48	27	50	29	58	37

From the results obtained the following conclusions can be drawn.

- Both crack initiation and crack propagation resistance decrease with increasing crosslinking which occurred due to the use of excess diisocyanate. This is thought to be due to the higher modulus and lower extension at break ability of the more highly crosslink polyurethane.
- It is found that the relationship between fatigue life and applied strain is similar to the "Wohler curve".
- Internal heat generation of these polymers was also found to increase with increasing excess percentage diisocyanate and the percentage of applied strain.
- The temperature of these polymers sharply increased during the first five minutes of flexing and then remained approximately constant.

***Figure 3:** Heat generation against time for polyurethane elastomers based on Capa 225/CHDI / 1, 4 – BD + 1, 4 – CHDM with different amounts of excess CHDI at 100% strain*

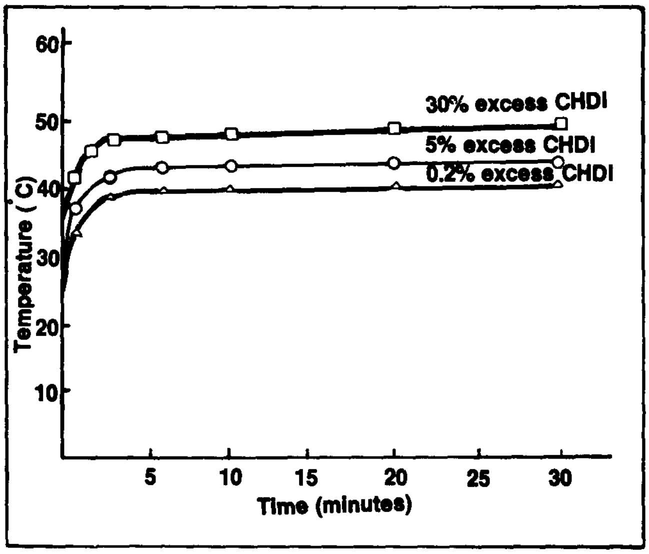
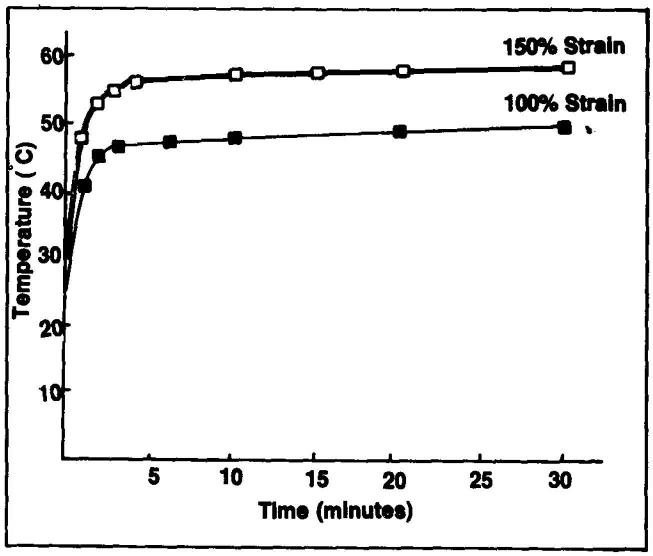


***Figure 4:** Heat generation against time of polyurethane elastomers based on Capa 225/CHDI / 1, 4 – BD + 1, 4 – CHDM with 30% excess CHDI at different % strain*



REFERENCES

[1] Barikani, M. and Hepburn C., "The Relative Thermal Stability of Polyurethane Elastomers: Effect of Diisocyanate Structure", Cellular Polymers, 6(2), 1987, 41 – 54.

[2] Barikani M. and Hepburn C., "The Relative Thermal Stability of Polyurethane Elastomers: 2. Influence of Polyol - diisocyanate Molar Block Ratio with a Single and Mixed diisocyanate System", Cellular Polymers, 6 (1), 1987, 29 – 36.

[3] Barikani M. and Hepburn C., "Isocyanurate Crosslinking as a Means of Producing Thermally Stable Polyurethane Elastomers", Cellular Polymers, 5(3), 1986, 169 – 185.