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TECHNICAL REPORT No. 20

Polyurethane Elastomers Based on Hydroxyl - terminated Polybutadienes

B E Brokenbrow
D Sims
J Wright

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July
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Polyurethane Elastomers Based on Hydroxyl-terminated Polybutadienes

by

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SUMMARY

Polyurethane elastomers prepared from hydroxyl-terminated polybutadiene polymers and copolymers have been assessed and compared with polyester and polyether urethanes. The effects of various diols and diamines as chain extenders and crosslinking agents and additions of carbon black to the hydroxyl-terminated polybutadienes have also been studied.

Hydroxyl-terminated polybutadiene urethane elastomers showed superior hydrolytic stability to the polyester and polyether urethanes selected for comparison; on the other hand, their resistance to petroleum (STF) was less satisfactory.

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Reference: WAC/207/03

1 INTRODUCTION

Polyurethane elastomers are usually prepared by reacting di- or polyfunctional hydroxyl-terminated polyesters or polyethers with di- or polyfunctional isocyanates. In general, polyurethane elastomers have good mechanical and electrical properties and show good resistance to oxygen, ozone and dry air at temperatures up to 75°C.

The properties of polyurethane elastomers may vary quite widely depending on their molecular weight, degree of crosslinking, intermolecular forces, stiffness of chain units, ease of rotation of chain segments and crystallinity. Polyurethane elastomers, however, suffer from certain inherent limitations. Polyester urethanes, for example, are sensitive to hydrolysis and solvent attack, while polyether urethanes are also susceptible to photo-oxidative degradation.

A possible way of overcoming some of these disadvantages might be to replace the polyester or polyether component with a medium molecular weight di- or polyhydroxyl-bearing hydrocarbon polymer such as polyisoprene or polybutadiene.

Although hydroxyl-terminated hydrocarbon homopolymers have been reported in the literature,[1,2,3,4,5] hydroxyl-terminated butadiene homopolymers and copolymers with styrene and acrylonitrile, having molecular weights of over 2000, have only been available commercially in the United States since 1965.[6] According to French[7] four commercial organisations in the United States supplied hydroxyl-terminated polybutadienes during 1968. Two of these organisations used an ionic polymerisation method of preparation and two a free radical method.

The object of the present investigation was to assess four hydroxyl-terminated butadiene homopolymers and copolymers, supplied by Sinclair Petrochemicals Inc US, as components of polyurethane elastomers and to study their ageing characteristics after immersion in water and petrol (STF).

2 MATERIALS

The materials evaluated, of average molecular weight 2500 - 3500 with a hydroxyl functionality of 2.1 to 2.6, were as follows.

R.15M and R.45M	hydroxyl-terminated polybutadiene homopolymers
CS.15	a hydroxyl-terminated polybutadiene/styrene copolymer
CN.15	a hydroxyl-terminated polybutadiene/acrylonitrile copolymer

The properties of the materials supplied are listed in Table 1 below.

TABLE 1

	R.15M Butadiene Homopolymer	R.45 M Butadiene Homopolymer	CS.15 Styrene Copolymer	CN.15 Acrylonitrile Copolymer
*Hydroxyl No (KOH mg/g)	38	43	36.5	32
**Hydroxyl Value (meq/g)	0.68	0.75	0.65	0.57
**Equivalent Weight	1470	1330	1540	1780
Viscosity, poise (30°C)	225	55	205	490
Non-volatile (4 h - 100°C)	99.9	99.9	99.5	99.5
Colour Visual	pale lemon	pale lemon	opaque white	orange

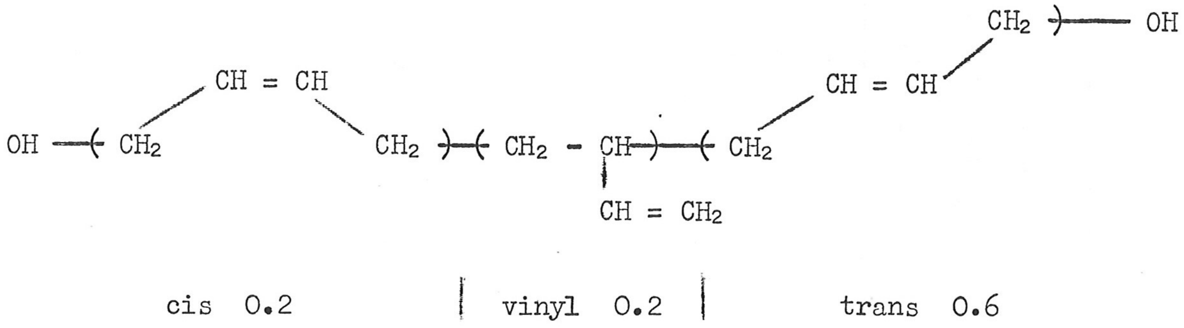
*Determined

**Calculated Hydroxyl value, millilitres equivalent per g $= \frac{\text{Hydroxyl No}}{56.1}$

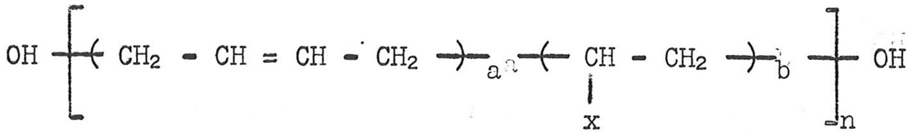
Equivalent weight $= \frac{1000}{\text{Hydroxyl Value}}$

The structures of the materials are as follows.

R.15 M and R.45 M homopolymers



CS.15 and CN.15 copolymers



$$OH - \left[(CH_2 - CH = CH - CH_2)_a - (\underset{x}{\underset{|}{CH}} - CH_2)_b \right]_n - OH$$

where x is phenyl for CS.15 butadiene/styrene copolymer

a = 0.85
b = 0.25
n = 40 - 50

or

where x is CN for CN.15 butadiene/acrylonitrile copolymer

a = 0.85
b = 0.15
n = 55 - 65

The polybutadiene microstructure of all the polymers is

trans - 1,4 60%, cis - 1,4 20%, vinyl 1,2 20%

3 GENERAL METHODS OF ELASTOMER PREPARATION

All the elastomers were prepared using toluene di-isocyanate (TDI)-Hylene T.M. supplied by Du Pont UK - a mixture of 80 per cent 2,4 and 20 per cent 2,6 isomers. Details of the elastomers are summarised in Table 2, detailed formulations and methods of preparation are given in Appendix B.

TABLE 2A

Hydroxyl-terminated Polybutadiene Elastomers P.1 - P.16

	Prepolymer		Elastomer		
Elastomer Number	Hydroxyl-terminated Polybutadiene	Ratio	Diol	Diamine	Carbon Black (a) (parts per hundred prepolymer)
		NCO : OH	NCO : OH 1.1 : 1.0	NCO : NH 0.7 : 1.0	
P.1	R.45	1.0 : 1.0	-	-	-
P.2	R.15	1.0 : 1.0	-	-	-
P.3	R.15	1.09 : 1.0	2-ethyl hexane-1,3-diol**	-	-
P.4	R.45	1.08 : 1.0	" **	-	-
P.5*	R.45	1.08 : 1.0	"	-	-
P.6	R.15	1.09 : 1.0	"	-	-
P.7	CS.15	1.09 : 1.0	"	-	-
P.8	CN.15	1.09 : 1.0	"	-	-
P.9	R.45	1.08 : 1.0	1,4-butane diol	-	-
P.10	R.45	1.08 : 1.0	1,5-pentane diol	-	-
P.11	R.45	1.08 : 1.0	1,2-propane diol	-	-
P.12	R.45	1.08 : 1.0	2-ethyl hexane-1,3-diol	-	-
P.13	CS.15	1.09 : 1.0	-	Flexzone 4L (b)	-
P.14	CN.15	1.09 : 1.0	-	"	-
P.15	R.15	1.09 : 1.0	2-ethyl hexane-1,3-diol	-	16
P.16	CN.15	1.09 : 1.0	"	-	16

(a) Vulcan 3F carbon black

(b) N,N'-bis-(4-dimethylpentyl)-p-phenylenediamine

* Elastomer prepared using dibutyl tin dilaurate

** P.3. Diol NCO : OH 1.3 : 1.0; P.4, 1.0 : 1.0

TABLE 2B

Polyether and Polyester Elastomers P.17 - P.24

Elastomer Number	Polyester	Moles	Polyether	Moles	Diol, Diamine or, Triol	Moles	TDI Moles
P.17	Diethylene adipate (mol wt 2000)	1.0	-	-	1,2,6-hexane triol	0.66	2.2
P.18	-	-	Propylene glycol (mol wt 2000)	1.0	1,2,6-hexane triol	0.67	2.33
P.19	Diethylene adipate (mol wt 2000)	1.0	-	-	butadiene epichlorhydrin	0.40	2.1
P.20	Diethylene adipate (mol wt 2000)	1.0	-	-	styrene epichlorhydrin	0.50	2.2
P.21	-	-	Tetramethylene glycol (mol wt 1970)	1.0	1,2,6-hexane triol	0.66	2.2
P.22	-	-	Tetramethylene glycol (mol wt 1970)	1.0	MOCA*	*8.8 pph	2.06
P.23	Diethylene adipate (mol wt 2200)	1.0	-	-	1,2,6-hexane triol	0.66	2.1
P.24	Tetramethylene adipate (mol wt 2250)	1.0	-	-	1,2,6-hexane triol	0.66	2.1

*4,4'-methylene-bis-(2-chloroaniline) 8.8 parts per hundred of prepolymer

3.1 Elastomers P.1 - P.16 Based on Hydroxyl-terminated Polybutadiene Homopolymers and Copolymers

3.1.1 Elastomers P.1 and P.2

These were prepared by direct reaction between the hydroxyl-terminated polybutadiene polymers and TDI to give an NCO : OH ratio of 1.0 : 1.0.

3.1.2 Elastomers P.3 - P.16

These elastomers were prepared by a prepolymer method. The hydroxyl-terminated polybutadiene polymer, 1 mole, was reacted with TDI, 2.1 - 2.6 moles, to produce an isocyanate-terminated prepolymer with a free NCO content of 6 - 9 per cent. The prepolymers, with or without the addition of carbon black, were subsequently reacted with diols or diamines to give an NCO : OH ratio of 1.1 : 1.0 or NCO : NH ratio of 0.7 : 1.0.

3.2 Elastomers P.17 - P.24 Based on Polyethers and Polyesters

Polyesters (average molecular weight 2000, acid number < 1.0, hydroxyl number 55 - 65), were prepared in the laboratory by the reaction between diethylene or tetramethylene glycol and adipic acid.

Polyethers based on polypropylene and polytetramethylene glycols (average molecular weight 2000, acid number < 1.0, hydroxyl number 55 - 65), were obtained from commercial sources.

Most of the elastomers were prepared by a direct method in which 1 mole of polyester or polyether and 0.66 mole 1,2,6-hexane triol crosslinking agent was reacted with 2.1 to 2.2 moles of TDI. A few elastomers were prepared using polyether or polyester/TDI prepolymers and chain extended or crosslinked with experimental hydroxyl-bearing low molecular weight butadiene-epichlorhydrin or styrene-epichlorhydrin polymers, or alternatively 4,4'-methylene-bis-(2-chloroaniline).

3.3 Preparation of Elastomer Sheet

The reaction products were poured into PTFE coated steel trays and cured in an oven for 60 h at 70 - 90°C to produce sheets 220 x 150 mm, 2.5 mm thick. The casting properties and general appearances of the hydroxyl-terminated polybutadiene elastomers are summarised in Table 3.

TABLE 3

Elastomer Number	General appearance of elastomer
P.1	Good - pale yellow - no bubbles
P.2	" " " " "
P.3	" " " " "
P.4	" " " " "
P.5	Slightly overcured - ridges
P.6	Fair-good - pale orange - a few bubbles
P.7	Good - pale yellow - a few bubbles
P.8	" " " " "
P.9	Slightly incompatible - opaque white - no bubbles
P.10	Good - yellow - slow curing
P.11	Slightly incompatible - opaque white - no bubbles
P.12	Good - yellow - no bubbles
P.13	Fair - brown-black - isolated bubbles
P.14	" " " " "
P.15	Fair - black - some ridges - isolated bubbles
P.16	Fair - black - some ridges and bubbles

4 EXPERIMENTAL

British Standard type E dumb-bell test pieces (eight) were cut from the cast sheets and the width and thickness measured before exposure to the test conditions. Dumb-bells, in sets of four, were suspended in loosely stoppered glass tubes and exposed to some or all of the following environments for twenty-eight days.

Controls	Conditioned in air at 20°C
Hot/dry	Suspended in air at 80°C
Hot/wet	Immersed in boiled out distilled water at 80°C
*Standard Test Fluid	Immersed in Standard Test Fluid at 65°C according to BS 903 : Part A 16

The charged tubes were placed in circulating air ovens in which the temperature did not vary by more than ± 0.5°C from the test temperature. After twenty-eight days' exposure the tubes and contents were removed from the oven and conditioned at room temperature for 24 hours before testing. After the conditioning period, the groups of four specimens were removed from the tubes, dried from a superficial liquid, and tested for hardness, moduli, extension at break and tensile-strength as quickly as possible. Hardness was measured using a micro-indentometer and the tensile properties on a Hounsfield Tensometer by British Standard Methods.[9,10] Unaged control specimens cut from the materials were tested by the same methods, and the results used as "unaged" reference points.

5 RESULTS AND DISCUSSION

The mechanical properties of the elastomers before ageing for twenty-eight days are recorded in Table 4, Appendix A.

The percentage changes in the original mechanical properties of the elastomers after ageing are recorded in Table 5, Appendix A.

Many of the hydroxyl-terminated polybutadiene urethane elastomers possessed good hydrolytic stability, showing changes in hardness, moduli, tensile strength and extension at break, of less than 15 per cent after 28 days' immersion in water at 80°C. On the other hand, many of the polyester and polyether urethanes either disintegrated or showed considerable changes in original mechanical properties after immersion in water. Polyester urethanes P.19 and P.20 chain extended or crosslinked with experimental hydroxyl bearing butadiene-epichlorhydrin and methylstyrene-epichlorhydrin polymers were inferior to polyester urethanes prepared with conventional triols, for example, 1,2,6-hexane triol, especially after immersion in STF.

In general, the hydroxyl-terminated polybutadiene urethane elastomers were less satisfactory than the polyester and polyether urethanes in resisting STF at 65°C, as shown by the greater losses in tensile strength and extension at break of the

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*Standard Test Fluid (STF) consists of a 70/30 v/v mixture of iso-octane and toluene, and is intended to represent a standard "medium to high aromatics" content petrol.[8]

polybutadiene based elastomers.

5.1 Comparison of Polyurethanes based on Different Hydroxyl-Terminated Polybutadiene Polymers with Polyesters and Polyethers

Table 6 compares the initial mechanical properties and resistance to ageing of polyurethane elastomers prepared from four different hydroxyl-terminated polybutadiene polyurethane elastomers, all chain extended with 2-ethyl hexane-1,3-diol, with those of typical polyester and polyether urethanes.

Polyurethanes based on hydroxyl-terminated polybutadiene homopolymers, although having lower initial tensile strengths but similar hardness to the copolymers, showed the best all round resistance to water, judged by retention of their initial mechanical properties. Polyurethane elastomers prepared from hydroxyl-terminated polybutadiene homopolymers and copolymers were superior to polyester and polyether urethanes, although their resistance to STF was inferior.

5.2 Effect of Diols on the Properties of Hydroxyl-Terminated Polybutadienes Polyurethane Elastomers

Table 7 compares the initial mechanical properties and resistance to ageing of polyurethane elastomers prepared from a hydroxyl-terminated polybutadiene, chain extended with various diols.

Polyurethane elastomers based on a hydroxyl-terminated polybutadiene homopolymer, chain extended with a branched chain hydrocarbon 2-ethyl hexane-1,3-diol showed the best all round mechanical properties initially; elastomers based on 1,4-butane diol also showed good initial mechanical properties and were superior to elastomers based on 1,5-pentane and 1,2-propane diols. All the elastomers apart from those extended with 1,4-butane diol, judged by changes in their initial mechanical properties, showed satisfactory resistance to water. Elastomers based on 1,4-butane diol were not very satisfactory in water and also showed the greatest change after immersion in STF.

5.3 Comparison of Diol and Diamine Chain Extenders in Hydroxyl-terminated Polybutadiene Polyurethane Elastomers

Table 8 compares the initial mechanical properties and resistance to ageing of polyurethane elastomers based on hydroxyl-terminated butadiene/styrene and butadiene/acrylonitrile copolymers, chain extended with 2-ethyl hexane-1,3-diol and N,N'-bis-(dimethylpentyl)-p-phenylene diamine.

Elastomers based on hydroxyl-terminated polybutadiene copolymers, chain extended with diols, showed higher tensile strengths and extensions at break compared to those chain extended with diamines, although diamine extended elastomers were initially rather harder.

The water resistance of the diol extended elastomers, especially P.7 based on a butadiene/styrene copolymer, were superior to P.13 and P.14 chain extended with a diamine. In addition, the resistance of diol extended elastomers to STF was slightly better than those extended with diamines. The superior initial hardness of diamine extended elastomers, compared with those extended with diols, may be attributable to the fact that as the hydroxyl-terminated polybutadiene resins have a functionality exceeding two, crosslinking with diols would occur via allophanate and urethane reactions, while with diamines crosslinking via allophanate, biuret and urea reactions can occur. However, their inferior tensile strengths compared to diol extended elastomers is somewhat surprising, although it is likely that their properties could be improved by using a higher NCO : NH ratio.

5.4 Effect of Carbon Black Additions to Hydroxyl-Terminated Polybutadienes Polyurethane Elastomers

Table 9 compares the initial mechanical properties and resistance to ageing of polyurethane elastomers based on hydroxyl-terminated butadiene/styrene and butadiene/acrylonitrile copolymers, with and without the addition of carbon black.

Although no attempt was made to determine the optimum quantity or type of carbon black necessary to reinforce the elastomers, the addition of 16 parts per hundred carbon black to P.16, a butadiene-acrylonitrile/TDI prepolymer, appeared to be beneficial, both from the point of view of increasing tensile strength (by about 50 per cent) with relatively small losses of extension at break (about 20 per cent). Similarly the retention of mechanical properties of the carbon black filled elastomer after immersion in water was superior to those of the unfilled elastomer. Although no reinforcement was observed with P.15, a butadiene/styrene copolymer containing carbon black, the retention of tensile properties of this material after immersion in water were rather better than those of the unfilled elastomer.

TABLE 6

Elastomer Number	Type	Initial Properties			% change in mechanical properties after 28 days in					
		Tensile Strength, MN/m^2	Ext at break, %	Hardness, BS°	Water at 80°C			STF at 65°C		
					Tensile Strength	Extension at break	Hardness	Tensile Strength	Extension at break	Hardness
P.5	PBD homopolymer	7.8	355	80	- 2.6	-14.8	- 5.5	-85.4	-52.6	-62.5
P.6	PBD homopolymer	7.1	265	81	0.0	- 2.7	- 5.0	-84.8	-48.3	-55.4
P.7	PBD styrene copolymer	10.7	205	80	-16.3	-14.1	- 3.7	-82.6	-50.2	-35.0
P.8	PBD acrylonitrile copolymer	11.5	320	73	-38.0	-18.6	-15.5	-87.6	-58.1	-31.5
P.17	Polyester (polydiethylene adipate)	4.5	840	< 30	Disintegrated			-27.3	-11.3	0.0
P.24	Polyester (polytetramethylene adipate)	17.4	335	90	Disintegrated			-20.7	+10.1	- 5.5
P.18	Polyether (polypropylene glycol)	2.37	235	55	Disintegrated			-78.8	-62.2	0.0
P.22	Polyether (polytetramethylene glycol)	18.9	810	71	-97.8	-95.2	-57.8	- 5.8	+13.1	+ 2.8

TABLE 7

Elastomer Number	Type Diol	Initial Properties			% change in mechanical properties after 28 days in					
					Water at 80°C			STF at 65°C		
		Tensile Strength, MN/m^2	Ext at break, %	Hardness, BS°	Tensile Strength	Extension at break	Hardness	Tensile Strength	Extension at break	Hardness
P.9	1,4-butane diol	7.2	255	57	-47.1	+118	-28.1	-95.3	-52.9	-53.2
P.10	1,5-pentane diol	1.86	45	81	+10.0	-11.1	+ 4.9	-71.6	-44.4	-16.1
P.11	1,2-propane diol	3.03	105	81	+ 2.27	-65.1	0.0	-72.8	-58.0	-25.9
P.12	2-ethyl hexane-1,3-diol	7.2	210	78	- 3.7	- 9.4	- 2.6	-77.7	-54.3	-30.7

TABLE 8

Elastomer Number	Polymer and Chain Extender	Initial Properties			% change in mechanical properties after 28 days in					
					Water at 80°C			STF at 65°C		
		Tensile Strength, MN/m^2	Ext at Break, %	Hardness, BS°	Tensile Strength	Extension at break	Hardness	Tensile Strength	Extension at break	Hardness
P.7	Butadiene/styrene diol	10.7	205	80	-16.3	-14.1	- 3.7	-82.6	-50.2	-35.0
P.8	Butadiene/acrylonitrile diol	11.5	320	73	-38.0	-18.6	- 5.5	-87.6	-58.1	-31.5
P.13	Butadiene/styrene diamine	7.4	170	96	-47.1	+118	-28.1	-95.3	-52.9	-53.2
P.14	Butadiene/acrylonitrile diamine	7.2	195	87	-70.0	+120	-45.0	-95.8	-50.7	-45.0

TABLE 9

Elastomer Number	Polymer and chain extender	Carbon Black	Initial Properties			% change in mechanical properties after 28 days in					
						Water at 80°C			STF at 65°C		
			Tensile Strength, MN/m^2	Extension at break, %	Hardness, BS°	Tensile Strength	Extension at break	Hardness	Tensile Strength	Extension at break	Hardness
P.7	Butadiene/ styrene diol	Nil	10.7	205	80	-16.3	-14.1	- 5.0	-82.6	-50.2	-35.0
P.8	Butadiene/ acrylonitrile diol	Nil	11.5	320	73	-38.0	-18.6	- 5.5	-87.6	-58.1	-31.5
P.15	Butadiene/ styrene diol	16 pph	8.8	340	87	-11.8	- 8.8	-20.7	Too swollen to test		
P.16	Butadiene/ acrylonitrile diol	16 pph	16.5	255	83	- 5.1	- 2.7	- 7.2	-79.8	-45.6	-34.9

6 CONCLUSIONS

Hydroxyl-terminated polybutadiene homopolymers and copolymers are useful additional polyfunctional hydroxyl bearing components now available for the preparation of polyurethane elastomers. These materials appear to be of particular value in the formulation of polyurethane elastomers for applications where resistance to hydrolysis is important. The hydrolytic stability of polyurethane elastomers prepared from hydroxyl-terminated polybutadiene polymers, judged by laboratory tests, was superior to that of the polyester and polyether urethanes selected for comparison; however the resistance of the polybutadiene urethanes to petrol (STF) was less satisfactory. In this respect, urethane elastomers offering a compromise between acceptable hydrolytic and fluid stability might be achieved by blends of polytetramethylene glycol ether and polybutadiene homopolymers. In addition, the present investigation indicated that the performance and physical properties of polyurethane elastomers based on hydroxyl-terminated polybutadiene polymers could be upgraded by additions of carbon black and further investigations in this direction are also proposed. The long term outdoor durability of elastomers based on hydroxyl-terminated polybutadienes is being studied and the results will be reported at a later date, in conjunction with investigations which are at present being made at these laboratories, to correlate the performances of polyurethane elastomers with their chemical structure.

According to Richards,[1] who has prepared hydroxyl-terminated polybutadienes on a small scale at this Establishment, there would be little difficulty in scaling up the preparation for semi- or full commercial production should the need arise.

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APPENDIX A

MECHANICAL PROPERTIES

TABLE 4

Mechanical Properties of Polyurethane Elastomers (Unaged)

Elastomer		Tensile Strength, MN/m^2	Extension at break, %	Modulus at 100 per cent extension MN/m^2	Hardness, BS^o
Number	Type				
P.1	OH-PB	0.10	250	0.03	< 30
P.2	"	0.65	100	0.65	49
P.3	"	8.40	90	-	86
P.4	"	3.41	115	2.50	58
P.5	"	7.80	355	3.65	80
P.6	"	7.10	265	3.48	81
P.7	"	10.70	205	4.76	80
P.8	"	11.50	320	3.00	73
P.9	"	7.20	255	0.62	57
P.10	"	1.86	45	-	81
P.11	"	3.03	105	2.83	81
P.12	"	7.20	210	3.78	78
P.13	"	7.40	170	6.17	96
P.14	"	7.20	195	3.89	87
P.15	"	8.80	340	4.10	87
P.16	"	16.50	255	6.07	83
P.17	Polyester	4.50	840	0.03	< 30
P.18	Polyether	5.24	135	0.41	45
P.19	Polyester	2.37	235	0.76	55
P.20	"	1.41	255	0.34	44
P.21	Polyether	2.34	135	2.00	71
P.22	"	18.90	810	3.06	71
P.23	Polyester	1.72	350	0.30	30
P.24	"	17.40	335	10.70	90

OH-PB = Hydroxyl-terminated polybutadiene

APPENDIX A

TABLE 5

Percentage Changes of Original Mechanical Properties of Polyurethane Elastomers After Ageing

Elastomer No	% change after 28 days in											
	Dry air at 80°C				Water at 80°C				STF at 65°C			
	TS	E_B	H	M_{100}	TS	E_B	H	M_{100}	TS	E_B	H	M_{100}
P.1	+ 50.0	- 82.0	>+ 50.0	-	- 40.0	- 44.0	-	- 51.0	- 50.0	- 68.0	-	-
P.2	- 24.6	- 60.0	+ 20.4	-	- 40.0	- 20.0	+ 16.3	-	Too swollen to test			
P.3	- 10.7	- 33.3	+ 7.0	-	- 18.8	- 11.1	- 2.3	-	- 74.5	- 55.6	- 18.6	-
P.4	- 6.2	- 73.9	+ 53.5	-	- 57.8	- 25.2	- 3.5	-	- 95.9	- 34.8	-	-
P.5	-	-	-	-	- 2.6	- 14.8	- 5.5	- 2.0	- 85.4	- 52.6	- 62.5	- 80.0
P.6	-	-	-	-	0.0	- 2.7	- 5.0	+ 7.5	- 84.8	- 48.3	- 55.4	- 79.3
P.7	-	-	-	-	- 16.3	+ 14.1	- 3.7	+ 8.2	- 82.6	- 50.2	- 35.0	- 55.9
P.8	-	-	-	-	- 38.0	- 18.6	- 5.5	- 1.0	- 87.6	- 58.1	- 31.5	- 66.5
P.9	-	-	-	-	- 47.1	+118.0	- 28.1	- 38.7	- 95.3	- 52.9	- 53.2	-
P.10	-	-	-	-	+ 10.0	- 11.1	+ 4.9	-	- 71.6	- 44.4	- 16.1	-
P.11	-	-	-	-	+ 2.27	- 65.1	0.0	- 9.9	- 72.8	- 58.0	- 25.9	-
P.12	-	-	-	-	- 3.7	- 9.4	- 2.6		- 77.7	- 54.3	- 30.7	- 58.2
P.13	-	-	-	-	- 47.1	+118.0	- 28.1		- 95.3	- 52.9	- 53.2	-
P.14	-	-	-	-	- 70.0	+120.0	- 45.0		- 95.8	- 50.7	- 45.0	-
P.15	-	-	-	-	- 11.8	- 8.8	- 20.7		Too swollen to test			
P.16	-	-	-	-	- 5.1	- 2.7	- 7.2		- 79.8	- 45.6	- 34.9	- 84.0
P.17	+ 1.5	+ 12.5	-	-	Disintegrated				- 27.3	- 11.3	0.0	+165
P.18	- 77.5	+ 22.2	- 4.5	+100.0	Disintegrated				- 78.8	- 62.2	0.0	-
P.19	- 22.8	+ 29.8	- 31.0	- 88.2	Disintegrated				- 41.4	- 19.2	- 11.3	- 29
P.20	+ 2.1	+ 90.0	-	- 66.0	Disintegrated				- 51.5	- 27.5	- 18.2	- 3
P.21	+ 36.3	+ 78.1	- 2.8	-310	+ 14.4	+240.0	- 46.5	- 94	- 34.2	- 55.6	- 7.1	-
P.22	- 34.4	+ 32.8	+ 14.4	+ 35.3	- 97.8	- 95.2	- 57.8	-	- 5.8	+ 13.1	+ 2.8	+ 9.5
P.23	-	-	-	-	Disintegrated				- 92.4	- 31.5	-	-
P.24	-	-	-	-	Disintegrated				- 20.7	+ 10.1	- 5.5	- 81.3

P.1 - P.16 are hydroxyl-terminated polybutadiene urethanes

P.17, P.19, P.20, P.23 and P.24 are polyester urethanes

P.18, P.21 and P.22 are polyether urethanes

- = not tested or no value recorded

TS = Tensile strength at break, MN/m^2

E_B = Extension at break, %

H = Hardness, BS°

M_{10c} = Modulus at 100 per cent extension, MN/m^2

APPENDIX B

FORMULATIONS AND METHODS OF PREPARATION

HYDROXYL-TERMINATED POLYBUTADIENE ELASTOMERS P.1 AND P.2

	P.1	P.2
R.45 homopolymer	250 g	-
R.15 homopolymer	-	250 g
TDI 80% 2,4 isomer TDI 20% 2,6 isomer	16.25 g	14.75 g
**NCO : OH ratio	1.0 : 1.0	1.0 : 1.0

METHOD

To a 500 g one litre three-necked flask equipped with heating mantle stirrer, thermometer and vacuum inlet tube, was added 250 g hydroxyl-terminated polybutadiene polymer. The polymer was degassed at 25°C under 5 mmHg* vacuum and stirred continuously for 45 minutes.

TDI was added from a dropping funnel and the mixture stirred a further 15 minutes under vacuum.

**<u>Calculation</u>

$$\text{Wt/TDI per 100 g resin} = \frac{\text{Hydroxyl No Polybutadiene meq/g x Eq Wt TDI (NCO/OH ratio)}}{10}$$

---

* 1 mmHg = 133.322 N/m^2

TABLE 10

PREPARATION OF PREPOLYMERS P.P.1 - P.P.6 FOR ELASTOMERS P.3 - P.16

	P.P.1	P.P.2	P.P.3	P.P.4	P.P.5	P.P.6
R.45 M homopolymer	-	1000 g	1000 g	-	-	-
R.15 M homopolymer	1000 g	-	-	1000 g	-	-
CS.15 styrene copolymer	-	-	-	-	1000 g	-
CN.15 acrylonitrile copolymer	-	-	-	-	-	1000 g
TDI 80% 2,4 isomer) TDI 20% 2,6 isomer)	305 g	217 g	213 g	310 g	303 g	280 g
Unreacted NCO_2 content of prepolymer (calculated) %	9.1	6.0	8.25	9.0	9.0	8.7
Unreacted NCO (determined) %	-	-	8.33*	-	-	-
General appearance	pale lemon	pale lemon	pale lemon	pale lemon	opaque white	orange
Stability on storage	Cloudy 1 month	Cloudy 1 month	> 11month	> 1 month	> 1 month	skinning and thickening 1 month

METHOD

To a two-litre reaction flask, fitted with a detachable four-necked cover, equipped with heating mantle, stirrer, thermometer, and vacuum and nitrogen inlet tubes, was added 1000 g hydroxyl-terminated polybutadiene polymer. The temperature was raised to 110°C over 30 minutes and the resin degassed under 1 mmHg vacuum of 30 minutes. The resin was cooled to 25 - 30°C and TDI was added rapidly (2 to 3 minutes) under nitrogen and stirred continuously for 1 hour. The prepolymers were placed in dried 4 lb Kilner jars flushed with nitrogen and then sealed under nitrogen.

CALCULATION

Weight of TDI per 100 g Polybutadiene Resin =

$$\frac{(100)(\text{Equivalent weight of TDI})}{(\text{Equivalent weight Polybutadiene Resin})} \times \frac{100(\text{Equivalent weight NCO})}{100(\text{Equivalent weight NCO})}$$

$$\pm \frac{\text{Equivalent weight Polybutadiene})(\%\ \text{Free NCO})}{\text{Equivalent weight TDI} \qquad (\%\ \text{Free NCO})}$$

TABLE 11

Hydroxyl-Terminated Butadiene Polyurethane Elastomers

Elastomer Number	Polymer	Prepolymer Number	Free NCO in Prepolymer	Prepolymer, g	Diol	Diol, g	Diamine	Diamine, g	Mole Ratio NCO : OH or NH	**Carbon Black, g
P.3	R.15m	P.P.1	9.1	250	2-Ethyl hexane -1,3-diol	30.5	-		1.3 : 1.0	-
P.4	R.45m	P.P.2	6.0	250	" "	26.1	-		1.0 : 1.0	-
(a)P.5	R.45m	P.P.3	8.25	250	" "	32.5	-		1.1 : 1.0	-
P.6	R.15m	P.P.4	9.0	250	" "	35.5	-		1.1 : 1.0	-
P.7	CS.15	P.P.5	9.0	250	" "	35.5	-		1.1 : 1.0	-
P.8	CN.15	P.P.6	8.7	250	" "	34.4	-		1.1 : 1.0	-
P.9	R.45m	P.P.3	8.25	250	1,4-Butane diol	20.1	-		1.1 : 1.0	-
P.10	R.45m	P.P.3	8.25	250	1,5-Pentane diol	23.2	-		1.1 : 1.0	-
P.11	R.45m	P.P.3	8.25	250	1,2-Propane diol	35.5	-		1.1 : 1.0	-
P.12	R.45m	P.P.3	8.25	250	2-Ethyl hexane -1,3-diol	35.5	-		1.1 : 1.0	-
P.13	CS.15	P.P.5	9.0	250		-	Flexzone 4L*	54.3	0.75 : 1.0	-
P.14	CN.15	P.P.6	8.7	250		-	" "	52.5	0.75 : 1.0	-
P.15	R.15m	P.P.4	9.0	250	2-Ethyl hexane -1,3-diol	35.5	-		1.1 : 1.0	40.0
P.16	CN.15	P.P.6	8.7	250	" "	34.5	-		1.1 : 1.0	40.0

Note (a) 0.3 pph dibutyl tin dilaurate catalyst

* N,N'-bis-(1,4-dimethylpentyl)-p-phenylene diamine

** Vulcan 3F

Methods of Preparation

*P.P.3 - 12

To a 500 ml three-necked reaction flask equipped with heating mantle, stirrer, thermometer dropping funnel and vacuum inlet was added 250 g TDI/polybutadiene prepolymer. This was degassed under moderate vacuum (30 mmHg) for 30 minutes at 65°C. Dibutyl tin dilaurate catalyst was added to P.5 only. The temperature was raised to 75°C and the diol added under vacuum. The mixture was stirred continuously and degassed for 5 minutes under 1 mmHg vacuum.

P.P.13 - 14

Method as above, except the prepolymer was degassed at 25°C and diamine added under 1 mmHg vacuum.

P.P.15 - 16

Method as for .P.3 - 12, except that 40 g of carbon black was dispersed into 250 g of prepolymer prior to reaction at 65°C.

*Calculation:

$$\frac{\text{Weight of Diol or Diamine}}{\text{100 g Polybutadiene Prepolymer}} = \frac{(\%\text{ Free NCO in Prepolymer})\ (\text{Equivalent weight of Diol or Diamine})}{42(\text{NCO/OH or NH mole ratio})}$$

where Equivalent Weight of Diol or Diamine $= \frac{\text{Molecular weight}}{2}$

POLYESTER AND POLYETHER URETHANE ELASTOMER P.17 - P.24

The elastomers were prepared by a direct method, except for P.19, P.20 and P.22, which were prepared via a prepolymer method.

The polyesters (molecular weights 1900 - 2100) were prepared in the laboratory to give acid number < 1.0 mg KOH and hydroxyl number 55 - 65 mg KOH.[11] The adipic acid was laboratory reagent grade ex-BDH, melting point 152 - 154°C.

All the diols and triols used were laboratory reagent grades and were redistilled under reduced pressure before use.

The butadiene-epichlorhydrin and methyl styrene-epichlorhydrin oligomers were prepared in the laboratory.

The polyethers were obtained from commercial sources.

		Mol Wt	Moles	g
P.17	Polydiethylene adipate	2000	1.0	500.0
	1,2,6-hexane triol	134	0.66	22.0
	TDI	174	2.2	96.0
P.18	*Polypropylene glycol ether	2000	1.0	500.0
	1,2,6-hexane triol	134	0.67	22.5
	TDI	174	2.33	101.25
P.21	**Polytetramethylene glycol ether	1970	1.0	492.0
	1,2,6-hexane triol	134	0.66	22.0
	TDI	174	2.2	96.0
P.23	Polydiethylene adipate	2220	1.0	555.0
	1,2,6-hexane triol	134	0.66	22.0
	TDI	174	2.1	91.5
P.24	Polytetramethylene adipate	2250	1.0	562.0
	1,2,6-hexane triol	134	0.66	22.0
	TDI	174	2.1	91.5
P.22	Polytetramethylene glycol ether (2.8 per cent free NCO)			1000.0
	MOCA			88.0

*Ex-Union Carbide

**Polymeg ex-Quaker Oats Co

	Prepolymer	Mol Wt	Moles	g
P.19, P.20	Polydiethylene Adipate	2000	1.0	500
	TDI	174	2.1	91.5

METHOD

To a 1000 ml glass three-necked reactor equipped with mantle, thermometer, stirrer and nitrogen inlet tube was added 91.5 g TDI. The temperature was raised to 80°C and the polyester added over a period of 1 hour. The mixture was stirred under nitrogen for 3 hours at 85°C.

	P.19		P.20	
	Moles	g	Moles	g
Polydiethylene adipate/TDI prepolymer	5	120	2.2	133
Butadiene-epichlorhydrin oligomer	2	16	-	-
Methyl styrene-epichlorhydrin oligomer	-	-	1.0	42

METHOD

In a 250 ml three-necked glass reactor equipped with heating mantle, thermometer, stirrer and vacuum inlet tube was added the prepolymer; this was heated to 85°C with continuous stirring and degassed for 30 minutes under moderate vacuum, 30 mmHg. The chain extender was added and the mixture degassed for 3 minutes under 1 mmHg (P.19 at 85°C and P.20 at 120°C).

Technical Report No 20
Explosives Research and Development Establishment
POLYURETHANE ELASTOMERS BASED ON HYDROXYL-TERMINATED POLYBUTADIENES
Brokenbrow B E, Sims D, Wright J
July 1970
24 pp, 11 tabs, no figs

Polyurethane elastomers prepared from hydroxyl-terminated polybutadiene polymers and copolymers have been assessed and compared with polyester and polyether urethanes. The effects of various diols and diamines as chain extenders and crosslinking agents and additions of carbon black to the hydroxyl-terminated polybutadienes have also been studied.

Hydroxyl-terminated polybutadiene urethane elastomers showed superior hydrolytic stability to the polyester and polyether urethanes selected for comparison; on the other hand, their resistance to petroleum (STF) was less satisfactory.

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TECHNICAL REPORT No. 53

Relationships between Polyurethane Elastomer Structure and Ageing Properties: Part 2: Effect of Backbone Polyol

B E Brokenbrow
D Sims
J Wright

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Technical Report No 53

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Relationships between Polyurethane Elastomer Structure and Ageing Properties: Part 2: Effect of Backbone Polyol

by

B E Brokenbrow
D Sims
J Wright

SUMMARY

The effects of varying the backbone polyol on the properties of polyurethane elastomers have been investigated.

Unaged polyester urethanes, especially those based on polyethylene and polybutylene adipates (mol wt 2000), were generally tougher but considerably less resistant to hydrolysis than polyurethanes prepared from polyethers of similar molecular weights. Low molecular weight polyols (650 - 1260) led to more highly crosslinked elastomers with improved tensile strength, modulus, hardness, but with reduced flexibility.

Elastomers based on hydroxyl-terminated polybutadiene urethanes, and to a lesser extent polyoxybutylene glycol urethanes (mol wt 1300), showed the best resistance to hydrolysis at 80°C, while those based on polydiethylene adipate (mol wt 1000) and polyoxypropylene glycol (mol wt 1250) showed the best resistance to petrol (STF) at 65°C.

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Reference: WAC/207/034

1 INTRODUCTION

The effects of changes in the chemical structure of polyurethanes are being studied in order that elastomers possessing a satisfactory balance between resistance to ageing and initial mechanical properties may be prepared.

The first report of the present series[1] described the effect of varying the degree of crosslinking on the ageing properties of a typical polyether and a polyester urethane elastomer. It was shown that while unaged polyester urethanes gave the best mechanical properties, polyether urethanes showed superior hydrolytic stability. Optimum ageing properties were obtained with relatively highly crosslinked elastomers of M_c values (molecular weight per branch link) of about 2000.

The present investigation considers the effects of varying the backbone polyol on the ageing properties of polyurethane elastomers, using a variety of polyether and polyester polyols of molecular weights 650 - 2000 in toluene di-isocyanate (TDI) prepolymers crosslinked with 1,1',1''-trimethylol propane (TMP). In addition, a hydroxyl-terminated polybutadiene urethane elastomer, which had previously shown outstanding hydrolytic stability but rather poor resistance to petrol,[2] together with a hydroxyl-terminated polybutadiene-polyether blend, were assessed for comparison.

2 MATERIALS AND METHODS OF PREPARATION

All the elastomers were prepared via TDI prepolymers using the polyester, polyether and hydroxyl-terminated polybutadiene resins (acid number < 0.5, H_2O content < 0.02, average molecular weight 650 - 2000) listed in Table 1.

The polyols, which were either prepared in the laboratory or obtained from commercial sources, 1.0 mole equivalent were reacted with 2.1 moles equivalent TDI (toluene di-isocyanate, Hylene ex-Du Pont UK, an 80/20 mixture of 2,4 and 2,6 isomers) to give prepolymers containing 4.0 - 12.5 per cent free NCO and crosslinked with 0.66 moles equivalent of TMP (pure distilled). The methods of preparation are described in Appendix A.

TABLE 1

Elastomer Code No	Type	Backbone Polyol	Average Molecular Weight	Source of Polyol
S 20	Adipate Ester	Ethylene adipate	1000	Fomrez ex-Witco Chemical Co
S 22		Ethylene adipate	2000	" " "
S 23		Diethylene adipate	1000	" " "
S 23A		Diethylene adipate	2000	" " "
S 24		Propylene adipate	2000	" " "
S 25		Butylene adipate	2000	" " "
S 21	Mixed Adipate Ester	(Ethylene adipate (70%) ((Propylene adipate (30%)	2000	Laboratory prepared
S 27		(Butylene adipate (70%) ((Propylene adipate (30%)	2000	" " " "
S 33	Caprolactone Ester	ε-caprolactone/ diethylene glycol	2000	" "
S 30	Polyether	Polyoxypropylene glycol	1200	Union Carbide (UK) Ltd
S 26		Polyoxypropylene glycol	2000	" "
S 29		Polyoxybutylene glycol	650	'Polymeg' Quaker Oats Co
S 31		Polyoxybutylene glycol	1300	" " "
S 28		Polyoxybutylene glycol	2000	" " "
S 32A	Hydroxyl-terminated polybutadiene	R 15M		**Sinclair Petrochemicals
*S 32	Polyether-polybutadiene blend	R 15M 50%) Polyoxybutylene) Glycol 50%)	2250	**Sinclair Petrochemicals Quaker Oats Co

*Chain extended with 2-ethyl hexyl diol not crosslinked with TMP
**now Arco Chemical Co

3 EXPERIMENTAL

British Standard type C dumb-bell test pieces (four per test) were cut from the cast sheets and the width and thickness measured before exposure to the test conditions. Dumb-bells, in sets of four, were suspended in loosely stoppered glass tubes and exposed to some or all of the following environments for 28 days.

Controls	Conditioned in air at 20°C
Hot/dry	Suspended in air at 80°C
Hot/wet	Immersed in boiled out distilled water at 80°C
*Standard Test Fluid	Immersed in dry Standard Test Fluid at 65°C

The charged tubes were placed in circulating air ovens in which the temperatures did not vary by more than ± 0.5°C from the test temperature. After 28 days' exposure the tubes and contents were removed from the oven and conditioned at room temperature for 24 hours before testing. After the conditioning period, the groups of four specimens were removed from the tubes, dried from any superficial liquid, and tested for hardness, moduli, extension at break and tensile strength as quickly as possible. Hardness was measured using a micro-indentometer, and the tensile properties were measured by British Standard Methods[3,4] on a Hounsfield Tensometer. Unaged control specimens cut from the materials were tested by the same methods, and the results used as "unaged" reference points.

4 RESULTS AND DISCUSSION

The visual appearances of the elastomers before and after ageing are recorded in Table 7, Appendix B.

The mechanical properties after ageing are recorded in Table 8, Appendix B and the percentage changes in the original mechanical properties of the elastomers in Tables 4, 5 and 6.

4 1 Visual Appearance

The general condition of the urethane elastomers, both unaged and after ageing in water, STF and dry air, judged by visual and empirical methods of assessment and summarized in Table 7, Appendix B, are described below.

4 1 1 Initial Appearance

All the polyester urethane elastomers, apart from those based on polybutylene adipate and ϵ-caprolactone/glycol polyester which were slightly opalescent, were clear and colourless. Elastomers based on polyethylene and polybutylene

---

*Standard Test Fluid (STF) consists of a 70/30 v/v mixture of iso-octane and toluene, and is intended to represent a standard "medium to high aromatics" content petrol.[5]

adipates and ε-caprolactone were tough and flexible, while those based on poly-diethylene, propylene, ethylene/propylene and butylene/propylene adipate, while appearing to be less tough, were equally flexible.

Elastomers based on polyoxypropylene glycol were slightly opalescent, while those based on polyoxybutylene glycol were transparent but slightly yellow. The polyether elastomers appeared to be equally flexible as the polyester based elastomers but rather less tough; a notable exception was an elastomer based on a low molecular weight (650) polyoxybutylene glycol (S 29) which was tough and rigid. Elastomers based on an hydroxyl-terminated polybutadiene/ polyoxybutylene glycol blend (S 32) were yellow, moderately tough and flexible.

4 1 2 Exposure to Dry Air

All the polyester elastomers, apart from slight stiffening, appeared to be little affected by 28 days' exposure to dry air at 80°C, although all, with the exception of those based on polyethylene adipate, showed some yellowing.

Similarly polyether based elastomers, apart from showing rather more yellowing than the polyesters, appeared to be little affected by exposure to dry air. The elastomer based on a hydroxyl-terminated polybutadiene/polyether blend (S 32) showed considerable yellowing.

The yellowing of polyurethanes in the presence of oxygen is apparently governed by the oxidative processes of the products of degradation of the urethane groups. It is believed[6,7] that the thermal degradation of polyurethanes based on TDI takes place, like photolysis, at the -N-C- bonds with the evolution of CO_2 and the formation of amino groups, the oxidation of which leads to discolouration.

4 1 3 Water Immersion

After 28 days' immersion in water at 80°C all the polyester based urethane elastomers showed catastrophic failures and rapidly disintegrated into brown viscous liquids, their behaviour being identical to elastomers based on polybutylene adipate previously examined.[1] This shows that variations of chemical structure of polyester polyols have little effect on the hydrolytic stability of polyurethane elastomers under these admittedly drastic conditions of test.

On the other hand, polyether and polyether/hydroxyl-terminated polybutadiene based elastomers did not appear to be seriously affected by water immersion, those based on polyoxybutylene glycol being slightly better than those based on polyoxypropylene glycol.

4 1 4 STF (Petrol) Immersion

After 28 days' immersion in petrol at 65°C both polyester and polyether urethane elastomers appeared to be in fairly good condition. During the immersion period the polyether urethanes were rather more swollen than polyester elastomers but they rapidly recovered to their original dimensions after conditioning for 24 hours at room temperature.

Elastomers based on polydiethylene and polybutylene adipate, ϵ-caprolactone/glycol polyester and polyoxybutylene glycol showed the most discolouration.

4 2 Mechanical Properties

The mechanical properties of the elastomers before and after ageing are recorded in Table 8, Appendix B.

4 2 1 Initial Properties

There were considerable variations in the initial mechanical properties of urethane elastomers of similar crosslink density (Table 2). Tensile strengths varied from 1 - 30 MN/m² and in descending order of strength were those prepared from: polyethylene adipate, polybutylene adipate, ϵ-caprolactone/glycol polyester, mixed polyethylene and polybutylene/polypropylene adipates, hydroxyl-terminated polybutadiene/polyoxybutylene glycol blend, polyoxybutylene glycol, polydiethylene adipate and polyoxypropylene glycol.

Extensions at break varied from 165 per cent for elastomers based on polydiethylene adipate to around 350 per cent for those based on polyethylene adipate, ϵ-caprolactone/glycol polyester and a hydroxyl-terminated polybutadiene/polyether blend; the majority of polyether elastomers gave extension at break values of 180 - 225 per cent while the remainder of the polyester elastomers gave values of 250 - 300 per cent.

In general, polyester based urethane elastomers gave higher hardness values, 70 - 90 BS°, and 100 per cent moduli, 1.0 - 2.8 MN/m², than the polyethers which gave values of 45 - 75 BS° and 0.5 - 2.5 MN/m² respectively. The elastomer giving the highest hardness and 100 per cent modulus was S 25 based on polybutylene adipate which gave a value of 88 BS° and 2.8 MN/m², while S 26 based on polyoxypropylene glycol gave the lowest values, 46 BS° and 0.5 MN/m². Elastomers prepared from mixed polyester adipates, in general, provided a compromise between the properties of elastomers based on the individual polyesters.

The high tensile strength of urethanes based on polyethylene adipate is attributable to its ability to undergo reversible oriented crystallisation under stress,[8] therefore the higher mechanical strength of urethane elastomers based on crystalline or potentially crystallisable polymer intermediates is usually higher than that of elastomers based on amorphous polymers. The inferior tensile strength of elastomers prepared from polyoxypropylene glycol compared to polyoxybutylene glycol and most adipate esters is attributed to their irregular chain structure and lack of reversible crystallinity on extension and may also be due to the fact that about 4 per cent of the end groups of polyoxypropylene glycol of molecular weight 2000 are terminal olefinic groups which are unreactive towards isocyanates.

TABLE 2

EFFECT OF VARIATION OF BACKBONE POLYOLS (MOL WT 2000) ON PROPERTIES OF UNAGED POLYURETHANE ELASTOMERS

Type	Code No	Backbone Polyol	Tensile Strength (MN/m^2)	Extension at break (%)	Modulus MN/m^2 at 100% extension	Hardness BS°
Polyester	S 22	Ethylene adipate	24.9	350	1.9	71
	S 23A	Diethylene adipate	2.0	165	1.3	70
	S 24	Propylene adipate	4.8	265	0.9	65
	S 25	Butylene adipate	19.0	300	2.8	88
	S 21	Ethylene/propylene adipate	12.2	300	1.1	72
	S 27	Butylene/propylene adipate	8.4	300	1.3	73
	S 33	ϵ-caprolactone/ diethylene glycol	14.1	350	0.8	69
Polyether	S 26	Polyoxypropylene glycol	0.8	210	0.5	46
	S 28	Polyoxybutylene glycol	3.0	225	2.0	71
OH terminated Polybutadiene/ Polyether	S 32	Hydroxyl-terminated polybutadiene/ polyoxybutylene glycol	5.6	365	0.8	61
OH terminated Polybutadiene	S 32A	Hydroxy-terminated polybutadiene	7.1	265	3.5	81

Note 1 MN/m^2 = 143 lbf/in^2

The effects of reducing the molecular weight of the polyol backbone of urethane elastomers are shown in Table 3. The general effects on the mechanical properties of the unaged elastomers were as follows. With the exception of polyethylene adipate based urethanes, where reduction of molecular weight from 2000 to 1000 had little effect on the properties of the elastomer, tensile strength, modulus and hardness increased while extension at break, with exception of urethane based on polydiethylene adipate, decreased.

As mentioned above polyester based urethanes, because of their higher molar cohesive energies are generally stronger than polyether based elastomers of equivalent average molecular weight. Polyether based urethanes, using low molecular weight polyoxybutylene glycol of average molecular weight could give elastomers of similar ultimate tensile strengths although at the expense of a reduction in elongation at break. It is worth noting however that the form of the stress strain curve for polyethers would be quite different to that normally associated with polyesters.

TABLE 3

EFFECT OF VARYING THE MOLECULAR WEIGHT OF DIFFERENT BACKBONE POLYOLS ON THE PROPERTIES OF UNAGED POLYURETHANE ELASTOMERS

Type	Code No	Backbone Polyol	Average Mol Wt	Tensile Strength (MN/m^2)	Extension at break (%)	Modulus MN/m^2 at 100% extension	Hardness BS°
Polyester	S 20	Ethylene adipate	1000	23.8	250	2.8	67
	S 22	Ethylene adipate	2000	24.9	350	1.9	71
	S 23	Diethylene adipate	1000	8.6	190	3.1	74
	S 23A	Diethylene adipate	2000	2.0	165	1.3	70
Polyether	S 30	Polyoxypropylene glycol	1200	3.7	180	1.5	66
	S 26	Polyoxypropylene glycol	2000	0.8	210	0.5	46
	S 29	Polyoxybutylene glycol	650	24.7	150	12.6	81
	S 31	Polyoxybutylene glycol	1300	4.5	190	3.3	75
	S 28	Polyoxybutylene glycol	2000	3.0	225	2.0	71

4 2 2 Ageing in Dry Air

After 28 days' exposure to dry air at 80°C practically all the polyurethane elastomers showed increases in tensile strength and extension at break (Table 4). The elastomers showing the least change were those based on polyethylene adipate. The majority of elastomers of average molecular weight 2000 showed losses of 100 per cent modulus and hardness whereas the lower molecular weight elastomers gave increased values for hardness and 100 per cent modulus.

TABLE 4

EFFECT OF AGEING IN DRY AIR AT 80°C ON PHYSICAL PROPERTIES OF POLYURETHANE ELASTOMERS BASED ON DIFFERENT BACKBONE POLYOLS OF VARYING MOLECULAR WEIGHT

Type	Code No	Backbone polyol	Average Molecular Weight	Percentage change of original mechanical property			
				Tensile Strength	Extension at break	100% Modulus	Hardness
Polyester	S 20	Ethylene adipate	1000	+ 29	- 4	+95	+13.5
	S 22	Ethylene adipate	2000	+ 30	- 2.5	+ 5	- 3
	S 23	Diethylene adipate	1000	+ 90	+12.1	+20.4	+ 3.0
	S 23A	Diethylene adipate	2000	+ 5	+23	-28	- 4.5
	S 24	Propylene adipate	2000	+ 23	+11	-24	- 2
	S 25	Butylene adipate	2000	+ 4	+13	-66	-24
	S 21	Ethylene/propylene adipate	2000	+ 73	+11.5	-18	- 3
	S 27	Butylene/propylene adipate	2000	- 24	+ 3	-62	-12
	S 33	ϵ-caprolactone/diethylene glycol	2000	+ 10.5	+11.5	+60.5	-17.5
Polyether	S 30	Polyoxypropylene glycol	1200	+113.0	+43.0	+13	- 9
	S 26	Polyoxypropylene glycol	2000	+ 16.5	+16.0	-42	- 8.5
	S 29	Polyoxybutylene glycol	650	+ 16.0	+10.0	+25.5	0
	S 31	Polyoxybutylene glycol	1300	+ 52.5	+21	-54	-2.7
	S 28	Polyoxybutylene glycol	2000	- 35	+14	-43	-6
Poly-butadiene	S 32	Hydroxyl-terminated polybutadiene/ polyoxybutylene glycol	2000	- 5.5	-12.5	+50	-3

4 2 3 Water Immersion

After 28 days' immersion in water at 80°C (Table 5) it was impossible to determine the physical properties of the polyester urethane elastomers due to their catastrophic failures. The polyether urethanes were in fair condition; S 31 based on polyoxybutylene glycol showed a loss in tensile strength of 42 per cent and S 26 based on polyoxypropylene glycol showed a loss of tensile strength of 25 per cent. These materials were however inferior to S 32A a hydroxyl-terminated polybutadiene urethane which was virtually unaffected by water. S 32, a hydroxyl-terminated polybutadiene/polyether urethane blend, was not so satisfactory as when these polyols were used alone in urethane elastomers.

TABLE 5

EFFECT OF IMMERSION IN WATER AT 80°C ON PHYSICAL PROPERTIES OF POLYURETHANE ELASTOMERS BASED ON DIFFERENT BACKBONE POLYOLS OF VARYING MOLECULAR WEIGHT

Type	Code No	Backbone polyol	Average Molecular Weight	Percentage change of original mechanical property			
				Tensile Strength	Extension at break	100% Modulus	Hardness
Polyester	S 20	Ethylene adipate	1000	All disintegrated into brown viscous liquids			
	S 22	Ethylene adipate	2000				
	S 23	Diethylene adipate	1000				
	S 23A	Diethylene adipate	2000				
	S 24	Propylene adipate	2000				
	S 25	Butylene adipate	2000				
	S 21	Ethylene/propylene adipate	2000				
	S 27	Butylene/propylene adipate	2000				
	S 33	ϵ-caprolactone/diethylene glycol	2000				
Polyether	S 30	Propylene glycol ether	1200	-78	+65	-	-47
	S 26	Propylene glycol ether	2000	-25	+43	-60	-35
	S 29	Polyoxybutylene glycol	650	-68	+31	-84	- 9
	S 31	Polyoxybutylene glycol	1300	-42	+11	-70	-12
	S 28	Polyoxybutylene glycol	2000	-92	+97	-55	-10
Poly-butadiene	S 32A	Hydroxyl-terminated polybutadiene	2400	0.0	- 4	+ 6	- 4.0
	S 32	Hydroxyl-terminated polybutadiene/ polyoxybutylene glycol	2000	-77	-11	-50	-26

With polyether urethane elastomers a reduction in molecular weight of the backbone polyol led to a corresponding loss of hydrolytic stability which suggests that although crosslink density is increased, a high concentration of urethane groups is detrimental to the hydrolytic stability of polyether urethanes.

In comparing the hydrolytic stability of polypropylene and polybutylene adipate based elastomers with polyoxypropylene and polyoxybutylene glycols (Table 5) it would appear that the inferior hydrolytic stability of the polyesters is due to their acidity.

$$\text{Ester R.CO.O.R'} \xrightarrow[H_2O]{} \text{RCOOH} + \text{R'OH}$$

$$\text{Ether R.O.R'} \xrightarrow[H_2O]{} \text{ROH} + \text{R'OH}$$

It is likely that the hydrolysis of ester groups is autocatalysed by the carboxylic group formed on hydrolysis. Adipic acid released on hydrolysis causes autocatalytic decomposition and by using a water immersion test, as in the present investigation, no removal of decomposition products is possible as would be the case when ageing tests are made in conditions of high humidity.

Recent patents[9] describe polyurethane elastomers which it is claimed possess outstanding hydrolytic stability and were relatively unaffected by 21 days in water at 70°C (however the patent does not make it clear as to whether the elastomers were immersed in water or aged in humid air). The polyurethanes were prepared by ester exchange between diethyl adipate and 1,4-butylene glycol and reacted with diphenyl methane di-isocyanate and had acid numbers approaching zero. The use of polyester urethanes of this kind will be the subject of further investigation.

In spite of claims to the contrary[10,11] the hydrolytic stability of S33, a polyurethane based on ϵ-caprolactone/diethylene glycol polyester, was poor.

4 2 4 Petrol STF Immersion

Many of the elastomers were badly affected by immersion in STF. The elastomers least affected by petrol were based on S 23, polydiethylene adipate (mol wt 1000), and S 30, polyoxypropylene glycol (mol wt 1200). With the polyester urethanes a reduction in the molecular weight of the polyol improved petrol resistance, while for polyoxybutylene glycol urethanes the reverse effect was found. This effect has previously been noted[1] with urethanes of varying degree of crosslinking based on polyoxybutylene glycol.

TABLE 6

EFFECT OF IMMERSION IN PETROL (STF) ON PHYSICAL PROPERTIES OF POLYURETHANE ELASTOMERS BASED ON DIFFERENT BACKBONE POLYOLS OF VARYING MOLECULAR WEIGHT

Type	Code No	Backbone polyol	Average Molecular Weight	Percentage change of original mechanical property			
				Tensile Strength	Extension at break	100% Modulus	Hardness
Polyester	S 20	Ethylene adipate	1000	-76	-32	- 7	+12
	S 22	Ethylene adipate	2000	-83	-29	-48	- 1
	S 23	Diethylene adipate	1000	-33	-16	- 6	+ 1
	S 23A	Diethylene adipate	2000	-45	-35	-21	- 3
	S 24	Propylene adipate	2000	-81	-57	-22	- 5
	S 25	Butylene adipate	2000	-86	-37	-64	-25
	S 21	Ethylene/propylene adipate	2000	-85	-50	-18	- 4
	S 27	Butylene/propylene adipate	2000	-92	-65	-54	-16
	S 33	ε-caprolactone/diethylene glycol	2000	-85	-31	-63	-19
Polyether	S 30	Polyoxypropylene glycol	1200	-16	-56	-	-12
	S 26	Polyoxypropylene glycol	2000	+38	-52	-	-26
	S 29	Polyoxybutylene glycol	650	-79	-30	-62	- 2
	S 31	Polyoxybutylene glycol	1300	-55	-58	-	- 4
	S 28	Polyoxybutylene glycol	2000	-76	-71	-71	-10
Poly-butadiene	S 32	Hydroxyl-terminated polybutadiene/ polyoxybutylene glycol	2000	-75	-46	-38	-37

5 CONCLUSIONS

The properties of polyurethane elastomers prepared from toluene di-isocyanate/polyol prepolymers crosslinked with TMP varied considerably, being dependent on the particular backbone polyol used in the preparation of the prepolymer. Similarly, the molecular weights of the backbone polyols had considerable influence on the initial mechanical properties of the elastomers. No single backbone polyol was capable of conferring adequate resistance to the elastomers in all the selected environments.

In general, a decrease in the molecular weight of the backbone polyol led to more highly crosslinked elastomers with improved tensile strengths, modulus and hardness but with reduced flexibility. The more highly crosslinked polyether elastomers were usually the most stable to hydrolysis while the more highly crosslinked polyester urethanes were the more resistant to petrol. None of the elastomers based on polyesters were resistant to water at 80°C.

Elastomers based on polyoxybutylene glycol (mol wt 1300) were the most resistant to hydrolysis ether based materials, but these were rather inferior to elastomers based on hydroxyl-terminated polybutadienes. Attempts to improve the physical properties of hydroxyl-terminated polybutadiene based elastomers by blending with polyethers were not very successful.

Polyurethane elastomers based on polydiethylene adipate (mol wt 1000) and polyoxypropylene glycol (mol wt 1250) gave the best resistance to STF at 65°C. There was no marked difference in the resistance of polyether and polyester urethanes to dry air at 80°C.

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APPENDIX A

METHODS OF PREPARATION

ϵ-Caprolactone/Glycol Polyester

Pure redistilled anhydrous ethylene glycol, 40.1 g, and dibutyl tin dilaurate, 1.6 g, were heated to 50°C in a three-necked glass flask equipped with thermometer, stirrer, nitrogen-inlet, and equalising pressure dropping funnel to 150°C. ϵ-Caprolactone (pure), 1250 g, and dibutyl tin dilaurate, 3.2 g, were added over 1½ hours and the temperature of the mixture was allowed to rise to 180°C. Heating was continued under nitrogen with continuous stirring at 180 - 185°C for two hours. The acid number of the polymer was 0.73 and the hydroxyl number 49.2 giving an average molecular weight of 2200

Elastomers S 20 - S 33

All the elastomers were prepared via prepolymers as follows.

Toluene di-isocyanate (TDI), 2.1 mole equivalent, was placed into a dried 500 ml glass three-necked flask equipped with thermometer stirrer, nitrogen and vacuum-inlet and heated to 80°C under nitrogen. Melted polyol, 1.0 mole equivalent, previously degassed by heating to 120 - 125°C for 30 minutes and applying a vacuum of 1 mmHg* was added to the TDI over a period of 30 minutes. The mixture was heated under nitrogen with continuous stirring at 80 - 85°C for 3 hours; during the last 30 minutes a vacuum of 1 mmHg was applied.

The TDI prepolymer was transferred to a dried 600 ml beaker and degassed under 1 mmHg vacuum for 10 minutes. 1,1',1''-Trimethylol propane, 0.66 mole equivalent, was stirred into the prepolymer. The mixture was reheated to 80°C and degassed for 10 - 15 minutes at 1 mmHg.

The reaction products were poured into PTFE coated aluminium trays and cured in an oven for 16 h at 90°C to produce sheets 220 × 150 mm approximately 2.5 mm thick.

*1 mmHg = 133.322 N/m²

APPENDIX B

TABLE 7

GENERAL CONDITION AND APPEARANCE OF POLYURETHANE ELASTOMERS

	Code No	Elastomer and average molecular weight	Unaged	Water 28 days at 80°C	Dry Air 28 days at 80°C	STF 28 days at 65°C
POLYESTER	S 20	Ethylene adipate 1000	(transparent) tough and flexible	catastrophic failure, brown viscous liquid	(transparent) tough	(transparent) tough, slightly rigid
	S 22	Ethylene adipate 2000	- ditto -	catastrophic failure, amber viscous liquid	(transparent) tough	(transparent) tough, slightly rigid
	S 23	Diethylene adipate 1000	(transparent) fairly tough and flexible	catastrophic failure, dark brown viscous liquid	(slightly yellow) tough	(very slight yellowing) tough, slightly rigid
	S 23A	Diethylene adipate 2000	- ditto -	catastrophic failure, brown viscous liquid	(slightly yellow) slightly brittle	(very slight yellowing) tough, slightly rigid
	S 24	Propylene adipate 2000	- ditto -	catastrophic failure, dark brown viscous liquid	(slightly yellow) flexible	(transparent) weak, flexible
	S 25	Butylene adipate 2000	(opalescent, slightly yellow) tough and flexible	catastrophic failure, rubbery dark brown viscous liquid	(pale yellow) rigid	(slightly yellow) tough and flexible
	S 21	Ethylene/propylene adipate 7:3 2000	(transparent) fairly tough and flexible	catastrophic failure, brown viscous liquid	(transparent) flexible	(transparent) flexible
	S 27	Butylene/propylene adipate 7:3 2000	(very slightly opalescent) fairly tough and flexible	catastrophic failure, dark brown viscous liquid	(pale yellow) fairly tough	(very slight yellowing) flexible
	S 33	ϵ-caprolactone/diethylene glycol 2000	(slightly opalescent) tough and flexible	catastrophic failure, rubbery dark brown viscous liquid	(opalescent deep yellow) rigid	(slightly yellow) tough, flexible

TABLE 7 cont'd

	Code No	Elastomer and average molecular weight	Unaged	Water 28 days at 80°C	Dry Air 28 days at 80°C	STF 28 days at 65°C
POLYETHER	S 30	Polyoxypropylene glycol 1200	(slightly opalescent) moderately tough and flexible	(deep amber) slightly swollen, very flexible	(slightly yellow) slightly inflexible	(transparent) tough, flexible
	S 26	Polyoxypropylene glycol 2000	- ditto -	(amber) slightly swollen, weak and flexible	(pale yellow) flexible	(transparent) weak, flexible
	S 29	Polyoxybutylene glycol 650	transparent (slightly yellow) tough and rigid	(amber) rigid	(pale yellow) rigid	(very slight yellowing) rigid, inflexible
	S 31	Polyoxybutylene glycol 1300	transparent (slightly yellow) moderately tough and flexible	(amber) rigid	(pale yellow) fairly rigid	(very slight yellowing) rigid, inflexible
	S 28	Polyoxybutylene glycol 2000	- ditto -	(deep amber) brittle	(pale yellow) tough	(very slight yellowing) tough, flexible
BUTADIENE POLYETHER	S 32	Hydroxyl-terminated polybutadiene/ polyoxybutylene glycol ether 1:1 2000	(lemon yellow) moderately tough and flexible	(yellow) tough	(amber) tough	(deep amber) slightly swollen, flexible

TABLE 8

MECHANICAL PROPERTIES OF POLYURETHANE ELASTOMERS BEFORE AND AFTER TWENTY-EIGHT DAYS' AGEING

Code No	Polyol Type	Polyol	Av Mol Wt	Controls (unaged)						80°C Dry						80°C Wet						60°C STF					
				TS MN/m^2	EB %	H BS°	M (MN/m^2)			TS MN/m^2	EB %	H BS°	M (MN/m^2)			TS MN/m^2	EB %	H BS°	M (MN/m^2)			TS MN/m^2	EB %	H BS°	M (MN/m^2)		
							100%	200%	300%				100%	200%	300%				100%	200%	300%				100%	200%	300%
S 20	POLYESTER	Ethylene adipate	1000	23.8	250	67	2.8	8.2	-	30.7	240	76	5.5	16.6	-	Unable to test due to severe swelling and disintegration						5.7	170	75	2.6	-	-
S 22		Ethylene adipate	2000	24.9	350	71	1.9	3.2	7.4	32.6	340	69	2.0	2.3	4.9							4.1	250	70	1.0	2.6	-
S 23		Diethylene adipate	1000	8.6	190	74	3.1	-	-	16.3	215	76	3.7	12.0	-							5.8	160	75	2.9	-	-
S 23A		Diethylene adipate	2000	2.0	165	70	1.3	-	-	2.1	200	67	0.9	2.1	-							1.1	105	68	1.0	-	-
S 24		Propylene adipate	2000	4.8	265	65	0.9	2.5	-	5.9	295	64	0.7	2.1	-							0.9	115	62	0.7	-	-
S 25		Butylene adipate	2000	19.0	300	88	2.8	3.3	19.0	19.8	340	67	0.9	10.6	19.0							2.7	190	66	1.0	-	-
S 21		Ethylene/propylene adipate 7:3	2000	12.2	300	72	1.1	3.1	12.2	21.1	335	70	0.9	2.5	7.65							1.8	150	69	0.9	-	-
S 27		Butylene/propylene adipate 7:3	2000	8.4	300	73	1.3	2.7	8.4	6.4	310	64	0.5	1.6	6.4							0.7	105	61	0.6	-	-
S 33		ε-caprolactone/ diethylene glycol	2000	14.1	350	69	0.8	1.7	4.3	15.6	390	57	1.2	2.0	-							2.0	240	56	0.3	1.3	-

TABLE 8 cont'd

Code No	Polyol Type	Polyol	Av Mol Wt	Controls (unaged)						80°C Dry						80°C Wet						60°C STF					
				TS MN/m^2	EB %	H BS°	M (MN/m^2)			TS MN/m^2	EB %	H BS°	M (MN/m^2)			TS MN/m^2	EB %	H BS°	M (MN/m^2)			TS MN/m^2	EB %	H BS°	M (MN/m^2)		
							100%	200%	300%				100%	200%	300%				100%	200%	300%				100%	200%	300%
S 30	POLYMER	Propylene glycol ether	1200	3.7	180	66	1.5	-	-	8.0	260	60	1.7	4.5	-	0.8	300	35	0.2	0.3	0.8	3.1	80	58	-	-	-
S 26		Propylene glycol ether	2000	0.8	210	46	0.5	0.8	-	0.9	245	42	0.3	0.5	-	0.6	300	30	0.2	0.3	0.6	1.1	100	34	1.1	-	-
S 29		Polyoxybutylene glycol ether	650	24.7	150	81	12.6	-	-	28.6	165	81	15.8	-	-	8.0	195	74	2.0	-	-	5.3	105	79	4.8	-	-
S 31		Polyoxybutylene glycol ether	1300	4.5	190	75	2.3	-	-	6.8	230	73	1.8	4.0	-	2.6	210	66	1.0	2.4	-	2.0	80	72	-	-	-
S 28		Polyoxybutylene glycol ether	2000	3.0	225	71	2.0	2.5	-	1.95	256	67	0.7	1.4	-	0.25	440	64	0.45	1.2	2.6	0.7	65	64	-	-	-
S 32A	BUTADIENE	OH terminated polybutadiene	2400	7.1	265	81	3.5	5.7	-	-	-	-	-	-	-	7.1	255	78	3.7	5.8	-	1.1	135	37	0.7	-	-
S 32		OH terminated polybutadiene/ polyether	2200	5.6	365	61	0.8	1.7	3.0	5.3	320	59	1.2	2.2	4.4	1.3	325	45	0.4	0.7	1.3	1.4	200	38	0.5	-	-

KEY

TS = tensile strength

EB = extension at break

M = modulus

6.9 MN/m^2 = 1000 psi

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Elastomers based on hydroxyl-terminated polybutadiene urethanes, and to a

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Elastomers based on hydroxyl-terminated polybutadiene urethanes, and to a
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lesser extent polyoxybutylene glycol urethanes (mol wt 1300), showed the best resistance to hydrolysis at 80°C, while those based on polydiethylene adipate (mol wt 1000) and polyoxypropylene glycol (mol wt 1250) showed the best resistance to petrol (STF) at 65°C.

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B E Brokenbrow
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High Performance Polyurethane Elastomers:
Part 1: Laboratory Ageing Trials

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SUMMARY

A range of polyurethane elastomers based on di-isocyanate prepolymers of polyether, hydroxyl-terminated polybutadiene, polyester adipate and caprolactone polyols have been prepared and their ageing properties assessed under a wide variety of laboratory simulated environmental conditions, including exposure to dry air (80 - 100°C), ultraviolet radiation; immersion in oil at 100°C, STF (65°C) and water (50 - 100°C).

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SUMMARY

A range of polyurethane elastomers based on di-isocyanate prepolymers of polyether, hydroxyl-terminated polybutadiene, polyester adipate and caprolactone polyols have been prepared and their ageing properties assessed under a wide variety of laboratory simulated environmental conditions, including exposure to dry air (80 - 100°C), ultraviolet radiation; immersion in oil at 100°C, STF (65°C) and water (50 - 100°C).

Individual elastomers were capable of resisting many, but usually not all of these conditions, although certain urethane elastomers prepared from polyethers, average molecular weight 1000 - 2000, provided a reasonably acceptable compromise of properties under most conditions.

Elastomers based on hydroxyl-terminated polybutadiene/ modified 4,4'-diphenyl methane di-isocyanate prepolymers possessed initial mechanical properties which were superior to those prepared hitherto, whilst still retaining outstanding resistance to hydrolysis.

Polyester based urethane elastomers showed good resistance to dry air and fuels but their resistance to water at temperatures above 50°C was poor. The addition of polycarbodiimides slightly improved the water resistance of polyester urethanes, whilst ultraviolet absorbers in conjunction with an antioxidant pair, based on a mixture of butylated hydroxy propylene and dilauryl thiodipropionate, appeared to enhance the photo-oxidative stability of polyester urethanes.

1 INTRODUCTION

Previous investigations[1-5,12] by the present authors have shown that the ageing properties of polyurethane elastomers are strongly dependent on the chemical structure of the elastomer. For example, the type of backbone polyol, its molecular weight, the degree of crosslinking and the effective chemical group structure in the polymer chain had a marked influence on the initial physical properties of the unaged elastomers and their resistances to ageing when exposed to dry air, water and STF. Hydroxyl-terminated polybutadienes, for example, produced urethane elastomers with superior hydrolytic stability to elastomers prepared with conventional polyether and polyester backbone polyols.[2]

The main objective of the present investigation was to make practical use of the information obtained earlier and to prepare a series of polyurethane elastomers based on adipate and caprolactone esters, polyethers and hydroxyl-terminated polybutadiene polyols and assess their ageing characteristics under a wider range of laboratory simulated environmental conditions than hitherto examined. The effects of additives, including ultraviolet absorbers and antioxidants, would also be examined in those elastomers showing any marked shortcomings when exposed to a specific environment.

2 MATERIALS AND METHODS OF PREPARATION

Six laboratory prepared elastomers and one elastomer prepared from a commercially supplied polyether/toluene di-isocyanate prepolymer were evaluated.

Details of the formulations of elastomers are summarised in Table 1. The elastomers were prepared in 1000 g batches by the methods previously described in References 1 - 5.

TABLE 1

DETAILS OF ELASTOMERS SELECTED FOR AGEING TRIALS

Elastomer No	Polyol	OH functionality	Acid No mg KOH/g	Hydroxyl No Mg KOH/g	Water (per cent)	Average molecular weight	Moles equivalent	Di-isocyanate	Moles equivalent	Crosslinker/ chain extender	Moles equivalent
S 140	Hydroxyl-terminated butadiene (a)	2.5	0.0	43.0	0.1	3000	1.0	4,4'-diphenyl methane modified (b) (mol wt 288)	2.51	N,N'-bis-[2-hydroxy propyl aniline] (c)	1.25
S 147	ϵ-caprolactone ester (d)	2.0	0.3	56.1	0.03	2000	1.0	toluene (e)	2.20	1,1',1"-trimethylol propane, methylene-bis-(2-chloroaniline)	0.33 0.50
S 155	ϵ-caprolactone ester (f)	2.0	0.3	212.0	0.03	530	1.0	toluene (e)	2.10	1,4-butane diol, 1,1',1"-trimethylol propane	0.50
S 160	oxy 1,4-butylene glycol (h)	2.0	0.01	56.7	0.02	1980	1.0	toluene (e)	2.20	1,1',1"-trimethylol propane, methylene-bis-(2-chloroaniline)	0.33 0.50
S 173	oxy 1,4-butylene glycol (g)	2.0	0.01	109.4	0.01	1030	1.0	4,4'-diphenyl methane modified (b) (mol wt 288)	2.20	1,1',1"-trimethylol propane	1.0
S 176	Ethylene adipate 90% (i) Propylene adipate 10% (j)	2.0 2.0	0.42 0.55	59.0 59.0	0.02 0.01	1900	0.9 0.1	toluene (k)	2.20	1,1',1"-trimethylol propane, methylene-bis-(2-chloroaniline)	0.33 0.50
S 200	oxy 1,4-butylene glycol (l)	2.0	-	-	-	2000 (estimated)		toluene (e)	not known	4,4'-methylene bis-(2-chloroaniline)	1.32

(a) R45m ex-Arco Chemical Co

(b) Isonate 1432 ex-Upjohn Co

(c) Isonol C100 ex-Upjohn Co

(d) Niax D560 ex-Union Carbide Co

(e) Hylene T M 80%:20% 2,4:2,6 isomers ex-DuPont UK

(f) Niax D510 Union Carbide

(g) Polymeg 1000 ex-Quaker Oats Co

(h) Polymeg 2000 ex-Quaker Oats Co

(i) Formrez F7-37 ex-Witco Chemical Co

(j) Formrez F7-67 ex-Witco Chemical Co

(k) Hylene T 100% 2,4 isomer ex-DuPont UK

(l) Adiprene L83 ex-DuPont UK

3 EXPERIMENTAL

British Standard type C dumb-bell test specimens were cut from the cast sheets and the width and thickness measured before exposure to the test conditions. Dumb-bells in sets of five were suspended in loosely stoppered glass tubes and exposed to some or all of the following environments.

Controls	Conditioned in dry air at 20°C, 65 per cent rh for 28 days
Hot/dry	Suspended in dry air at 80°C for 28 days
Hot/dry	Suspended in dry air at 100°C for 28 days
Hot/wet	Suspended over water at 100°C for 14 days
Hot/wet	Immersed in water at 50°C for 28 days
Hot/wet	Immersed in water at 80°C for 14 days
Hot/wet	Immersed in water at 80°C for 28 days
*Standard Test Fluid (Petrol)	Immersed in STF at 65°C for 28 days
**ASTM Oil No 1	Immersed in oil at 100°C for 9 days

The charged tubes were placed in circulating air ovens in which the temperature did not vary by more than ± 0.5°C from the test temperature. After the required period of exposure the tubes and contents were removed from the oven and conditioned at room temperature for 24 hours before testing. After the conditioning period, the groups of five specimens were removed from the tubes, dried from any superficial liquid and tested for hardness, moduli, extension at break and tensile strength as quickly as possible. Hardness was measured using a micro-indentometer and the tensile properties were measured by British Standard Methods[6,7] on a Hounsfield Type E Tensometer at a constant rate of extension of 500 mm/min. Unaged control specimens cut from the elastomers were tested by the same methods, and the results used as 'unaged' reference points.

3 1 Ultraviolet Radiation

Dumb-bell specimens as described above were exposed in sets of 5 for 10 days to radiation from 2 kW high pressure xenon discharge lamp previously described.[9] The specimens were attached to cardboard frames moulded to and attached to the circumference of the inner wall surface of the drum. The temperature of the specimens was 29 - 31°C and the relative humidity of the air surrounding the specimens 34 - 36 per cent. The specimens were tested after exposure as in Section 3.

Note: *Standard Test Fluid (STF) consists of a 70/30 v/v mixture of iso-octane and toluene, and is intended to represent a standard medium to high aromatics content petrol.[8]

**ASTM Oil No 1 (ex-Esso Petroleum) is a petroleum based oil to ASTM Specification D471/57T, 1957.

3 2 Low Temperature Flexibility

The low temperature flexibility of the elastomers was determined by a method described recently[10] in which the torsional modulus of the material is determined as a function of temperature.

4 RESULTS AND DISCUSSION

4 1 Properties of Unmodified Polyurethane Elastomers

The results of mechanical tests and the percentage changes in original mechanical properties of the unmodified polyurethane elastomers after ageing are summarized in Table 2. Stress strain curves of the elastomers are reproduced in Figures 1 - 7. A histogram showing changes in the tensile strength of elastomers is reproduced in Figure 8.

4 1 1 S 140 Hydroxyl-Terminated Polybutadiene Urethane

This hydroxyl-terminated polybutadiene urethane elastomer was initially hard and rather inflexible giving a high 100 per cent modulus of 12.4 MN/m^2. The tensile strength of the elastomer, 16.7 MN/m^2, was almost double that previously reported[1] for hydroxyl-terminated polybutadiene/toluene di-isocyanate prepolymers crosslinked with diols such as 2-ethyl hexane 1,3-diol and 1,4-butane diol. This increase in strength is attributed to the introduction into the elastomer structure of the more bulky aromatic modified 4,4'-diphenyl methane di-isocyanate and N,N'-bis-[2-hydroxy propyl aniline] crosslinking agent.

The stress strain curve for the elastomer (Figure 1) is untypical of unfilled rubbery materials and indicates the elastomer to be relatively non-crystalline due to the absence of a region of strain hardening.

The elastomer showed outstanding hydrolytic stability being relatively unaffected by water at 50 - 100°C for periods up to 28 days. The effects of exposure to ultraviolet radiation and immersion in oil at 100°C were slight. During exposure to dry air at 80 and 100°C however, the elastomer stiffened as shown by losses of original extension at break of 55 - 65 per cent, whilst its tensile strength was practically unchanged.

The resistance of the elastomer, to STF (petrol) at 65°C for 28 days was poor as shown by the losses of tensile strength, elongation at break and hardness.

4 1 2 S 147 ϵ-Caprolactone Polyester Urethane (Ester MW 2000)

This elastomer was based on the higher molecular weight caprolactone polyester. This elastomer was a toluene di-isocyanate-terminated prepolymer crosslinked with MOCA/TMP. The elastomer gave satisfactory initial mechanical properties with a tensile strength of 26.1 MN/m^2 and an extension at break of 535 per cent. The stress strain curve for the elastomer (Figure 1) is typical of soft tough rubbery materials shows the elastomer to be relatively highly crystalline at stress levels above 10.0 MN/m^2. The elastomer had fairly good resistance to dry air at 80 and 100°C, although some stiffening was apparent, as shown by increases in tensile strength and losses of extension at break. However, the character of the stress strain curve (Figure 3) for the elastomer after heat ageing is basically similar to that of the unaged control.

Apart from elastomer S 200 based on a commercial polyether prepolymer, elastomer S 147 showed the greatest losses of original mechanical properties of all the unmodified elastomers examined after exposure to ultraviolet radiation. The elastomer stiffened after immersion in oil at 100°C and showed considerable losses of extension at break and tensile strength after 28 days' immersion in STF at 65°C.

The hydrolytic stability of the elastomer S 147 was reasonable after 28 days' immersion in water at 50°C and after 14 days at 80°C. However, after 28 days at 80°C and 14 days at 100°C the elastomer was severely degraded by water, thus confirming our previous observations[3] of the limited hydrolytic stability at elevated temperatures of urethane elastomers prepared from caprolactone polyesters.

4 1 3 S 155 ε-Caprolactone Polyester Urethane (Ester MW 500)

Elastomer S 155 was prepared from a relatively low molecular weight caprolactone polyester/toluene di-isocyanate prepolymer cured with a diol/triol blend. Nevertheless, the unaged elastomer gave good mechanical properties with a tensile strength of 40.0 MN/m^2 and an extension at break of 300 per cent.

The stress strain curve for the elastomer (Figure 1) is typical of hard strong crystalline rubbery materials.

After exposures to dry air at 80 - 100°C (Figure 4), ultraviolet radiation and oil at 100°C the elastomer stiffened appreciably as shown by increases in its 100 per cent modulus, suggesting that further crosslinking occurred during ageing.

The elastomer gave poor resistance to STF at 65°C and its hydrolytic stability was inferior to that of elastomer S 160 which was based on the higher molecular weight caprolactone ester.

4 1 4 S 160 Polyether Urethane (Ether MW 2000)

This polyurethane elastomer was based on a polyoxybutylene glycol/toluene di-isocyanate prepolymer, cured with a blend of TMP and MOCA. The unaged elastomer gave moderate mechanical properties although its initial tensile strength 11.6 MN/m^2 was comparatively low. The stress strain curve for the material (Figure 1) is almost linear and indicates that the elastomer is less crystalline than the elastomers based on the polycaprolactone esters.

After 28 days' ageing in dry air at 80°C the elastomer showed increased in both tensile strength and 100 per cent modulus, whilst after the same period at 100°C losses of tensile strength, extension at break and hardness occurred, which appears to confirm the opinion[5] that the upper operational temperature limit for polyether urethanes is in the region of 80°C.

Although the tensile strength of the elastomer was relatively unaffected by exposure to ultraviolet radiation, an increase in 100 per cent modulus occurred with considerable losses of extension at break. The elastomer also stiffened considerably after immersion in oil at 100°C. The elastomer showed fair resistance to STF after 28 days' immersion at 65°C and to water, after ageing for periods of 14 to 28 days at 50 - 100°C.

4 1 5 S 173 Polyether Urethane (Ether MW 1000)

This elastomer was based on the lower molecular weight polyoxybutylene glycol/ modified 4,4'-diphenyl methane di-isocyanate prepolymer crosslinked entirely with TMP.

The stress strain curve for the elastomer (Figure 1) shows the elastomer to be less flexible, but rather more crystalline, than the higher molecular weight polyether urethane S 160 described previously in Section 4 1 4.

The resistance of the elastomer to dry air at 80 and 100°C and to STF at 65°C was inferior to S 160 based on the higher molecular weight polyether, as shown by greater losses of original mechanical properties. Elastomer S 173 stiffened after exposure to ultraviolet radiation and immersion in oil at 100°C as shown by considerable increases in 100 per cent modulus and also by increases in tensile strength, especially after immersion in hot oil.

4 1 6 S 200 Commercial Polyether Urethane

This elastomer was based on a commercial polyoxybutylene glycol toluene di-isocyanate prepolymer, cured entirely with MOCA. Although the mechanical properties of the unaged elastomer were rather better than polyether urethanes S 160 and S 173, the resistance of the elastomer to water and STF was inferior to that of the experimental polyether urethane S 160. The elastomer showed relatively good resistance to dry air at 80°C and also to immersion in oil at 100°C.

4 1 7 S 176 Polyester Adipate Urethane (Ester MW 2000)

This elastomer was based on an ethylene/propylene 90:10 adipate ester/100 per cent 2,4 toluene di-isocyanate isomer prepolymer, cured with a blend of MOCA and TMP. The unaged elastomer showed good mechanical properties with a tensile strength of 32 MN/m² and an extension at break of 550 per cent. The stress strain curve of the elastomer (Figure 1) shows it to be a typical soft tough crystalline rubber similar to the other polyester urethanes examined, ie S 147 and S 155. The elastomer, apart from stiffening to some extent (Figure 7) showed satisfactory resistance to dry air at 80 and 100°C, ultraviolet radiation, oil at 100°C and STF at 65°C. Although the elastomer showed reasonably good resistance after 28 days' immersion in water at 50°C it was severely degraded after immersion at 80 and 100°C.

TABLE 2

CHANGES IN MECHANICAL PROPERTIES OF POLYURETHANE ELASTOMERS AFTER AGEING IN VARIOUS ENVIRONMENTS

Code No	Elastomer Type	Initial properties (unaged)				Percentage change of original mechanical property after ageing for																			
						28 days dry air (80°)				28 days dry air (100°C)				10 days ultraviolet				9 days oil (100°C)				28 days STF (65°C)			
		TS (MN/m^2)	M 100 (MN/m^2)	EB (%)	H (BS°)	TS	M 100	EB	H	TS	M 100	EB	H	TS	M 100	EB	H	TS	M 100	EB	H	TS	M 100	EB	H
S 140	Hydroxyl-terminated polybutadiene	16.7	12.4	175	97	- 3.6	-	-54.0	0	- 3.0	-	-63.0	0	- 6.5	+11.2	-29.0	0	- 30.0	- 32.0	- 17.0	-13.0	-74.0	-	-66.0	-35.0
S 147	ϵ-caprolactone ester (MW 2000)	26.1	3.1	535	87	+36.0	+ 19.0	-35.0	- 1.0	+ 8.0	-10.0	-21.0	-10.0	-26.0	+19.0	-43.0	-2.0	+ 28.0	+ 58.0	+ 93.0	+ 7.0	-66.0	+ 6.0	-42.0	- 5.0
S 155	ϵ-caprolactone polyester (MW 500)	40.7	7.1	310	82	+ 3.0	+135.0	-32.0	+21.0	+29.0	+94.0	-18.0	+21.0	+ 7.0	+82.0	-21.0	0	+ 40.0	+ 96.0	+ 6.0	+18.0	-65.0	-54.0	-18.0	- 9.0
S 160	Polyether (MW 2000)	11.6	4.3	355	89	+52.0	+ 21.0	- 7.0	- 3.0	-24.0	+ 3.0	-24.0	- 9.0	- 3.0	+16.0	-47.0	-1.0	+133.0	- 9.0	+ 79.0	- 3.0	-31.0	+23.0	-49.0	-11.0
S 173	Polyether (MW 1000)	14.1	4.6	180	82	- 7.0	-	-47.0	+ 9.0	-26.0	-	-47.0	+ 4.0	+11.0	+91.0	-28.0	-1.0	+134.0	+176.0	- 3.0	+ 6.0	-66.0	-	-53.0	- 2.0
S 200	Polyether (commercial)	17.6	4.0	420	88	+19.0	+ 4.0	+25.0	- 7.0	-	-	-	-	-34.1	0	-33.3	0	+ 5.0	- 95.0	+120.0	- 7.0	-62.0	- 4.0	-32.0	0
S 176	Polyester adipate (MW 2000)	32.2	3.6	555	88	+32.0	+ 28.0	-24.0	- 2.0	- 7.0	-25.0	- 8.0	- 7.0	+ 2.0	+31.0	-32.0	+1.0	+ 37.0	- 6.0	+ 62.0	- 5.0	-20.0	+ 6.0	-30.0	- 1.0

TABLE 2 (Contd)

Code No	Elastomer Type	Initial properties (unaged)				Percentage change of original mechanical property after ageing for															
						28 days water (50°C)				14 days water (80°C)				28 days water (80°C)				14 days water (100°C)			
		TS (MN/m²)	M 100 (MN/m 2)	EB (%)	H (BS°)	TS	M 100	EB	H	TS	M 100	EB	H	TS	M 100	EB	H	TS	M 100	EB	H
S 140	Hydroxyl-terminated polybutadiene	16.7	12.4	175	97	+12.0	+25.0	-23.0	0	- 0.6	+23.0	-26.0	0	+12.0	+ 6.6	-23.0	0	0	+17.0	-20.0	0
S 147	ϵ-caprolactone polyester (MW 2000)	26.1	3.1	535	87	-30.0	+ 6.0	-34.0	- 1.0	-18.0	+71.0	+52.0	+ 1.0	Disintegrated				Disintegrated			
S 155	ϵ-caprolactone polyester (MW 500)	40.7	7.1	310	82	-55.0	-55.0	-29.0	- 7.0	-84.0	-72.0	- 8.0	-22.0	-97.0	-94.0	+ 3.0	-66.0	Disintegrated			
S 160	Polyether (MW 2000)	11.6	4.3	355	89	+27.0	+ 7.0	-10.0	0	+41.0	-16.0	+93.0	- 7.0	+40.0	-49.0	+69.0	- 9.0	-24.0	-67.0	+93.0	-34.0
S 173	Polyether (MW 1000)	14.1	4.6	180	82	-38.0	+57.0	-39.0	0	-21.0	0	-11.0	0	-29.0	- 4.0	-17.0	- 4.0	-41.0	-35.0	0	-20.0
S 200	Polyether (commercial)	17.6	4.0	420	88	-	-	-	-	-61.0	-79.0	+44.0	-21.0	-61.0	-79.0	+44.0	-21.0	-97.0	-	-98.0	-91.0
S 176	Polyester (MW 2000)	32.2	3.6	555	88	-11.0	+34.0	-23.0	-17.0	Too soft to test				Disintegrated				Too soft to test			

Key:
TS = tensile strength at break
M100 = modulus at 100 per cent extension
EB = percentage extension at break
H = hardness
\- = not tested or no value obtained
MW = average molecular weight (nominal)

4 2 Properties of Polyurethane Elastomers Prepared with Alternative Chain Extenders and Crosslinking Agents (Methods of Cure)

In an attempt to improve certain of the properties of the unmodified polyurethane elastomers described in Section 4 1, the use of alternative crosslinking and chain extending agents to those used in these elastomers was investigated. Apart from these changes, the formulations of the elastomers and the methods of test were the same as those described in Sections 2 and 3.

Details of the alternative curing systems, the mechanical properties of the unaged elastomers and the percentage changes in original mechanical properties of the elastomers after ageing are summarised in Table 3. The results are compared with those of Table 2 in the discussion below.

4 2 1 Hydroxyl-Terminated Polybutadiene Urethanes

Elastomer S 143 was identical to S 140 based on a hydroxyl-terminated polybutadiene, except that the N,N'-bis-(2-hydroxy propyl aniline) was replaced with 2-ethyl hexane 1,3-diol.

This replacement gave an elastomer with greater extension at break with little sacrifice in other properties. However the resistance to STF was not improved and remained unsatisfactory.

4 2 2 ϵ-Caprolactone Polyester Urethanes (Ester MW 2000)

The MOCA/TMP cure of elastomer S 147 was replaced with 100 per cent MOCA in S 148, and with 100 per cent TMP in S 152.

In elastomer S 148 the effect of a 100% MOCA cure was to produce further improvements in the already satisfactory initial mechanical properties. Although a slight improvement in resistance to dry air at 80°C was achieved the resistance of the elastomer to STF at 65°C and water at 80°C remained poor.

The effect of introducing 100 per cent TMP cure into elastomer S 151 was to produce a much softer elastomer than the MOCA/TMP cured material, with inferior ageing properties compared to elastomer S 147. These results confirm those already obtained from TMP cured polyesters.[12]

4 2 3 ϵ-Caprolactone Polyester Urethanes (Ester MW 500)

S 154 elastomer was prepared using a MOCA/TMP cure. Although this alternative method of cure produced an elastomer with slightly improved initial mechanical properties, the hydrolytic stability of the elastomer after immersion in water at 80°C remained poor.

4 2 4 Polyether Urethanes (Ether MW 2000)

In an attempt to improve the initial tensile strength of the elastomer S 160 and to reduce its tendency to stiffen during immersion in oil at 100°C, elastomers S 161 cured with 100 per cent MOCA and S 165 cured with 100 per cent N,N'-bis-(2-hydroxy propyl aniline) were prepared to compare with S 160 cured with a blend of MOCA and TMP. Elastomer S 161 gave improved initial mechanical properties with enhanced resistance to oil at 100°C; but its resistance to STF at 65°C and water at 80°C was inferior to that of the TMP/MOCA cured elastomer S 160. Elastomer S 165 cured with N,N'-bis-(2-hydroxy propyl aniline) was very soft and flexible initially and showed very poor resistance to STF at 65°C.

4 2 5 Polyether Urethane (Ether MW 1000)

Elastomer S 175 was prepared in which the TMP of S 173 was replaced with BD. This change should produce an elastomer with a more linear structure than that from a triol cure. The 1,4-butane diol cured elastomer was both more flexible and stronger than the triol cured elastomer S 173. In addition, the diol cured elastomer showed improved resistance to dry air and water at 80°C together with marginally improved resistance to STF at 65°C.

TABLE 3

EFFECT OF ALTERNATIVE CHAIN EXTENDERS/CROSSLINKING AGENTS ON AGEING PROPERTIES OF POLYURETHANE ELASTOMERS

Code No	Elastomer type	Crosslinking/ chain extending material	Initial properties (unaged)				Percentage change of original mechanical property after ageing for															
							28 days dry air (80°C)				9 days oil (100°C)				28 days water (80°C)				28 days STF (65°C)			
			TS (MN/m^2)	M 100 (MN/m^2)	EB (%)	H (BS°)	TS	M 100	EB	H	TS	M 100	EB	H	TS	M 100	EB	H	TS	M 100	EB	H
S 140	hydroxyl-terminated polybutadiene	hydroxy propyl aniline	16.7	12.4	175	97	- 3.6	-	-54.0	0	- 30.0	- 32.0	-17.0	-13.0	- 0.6	+23.0	-26.0	0	-74.0	-	-66.0	-35.0
S 143		2-ethyl hexyl 1,3-diol	15.8	10.2	255	97	+11.0	+ 64.0	-59.0	+ 1.0	- 27.0	- 15.0	-33.0	+23.0	0	+34.0	-53.0	0	-85.0	-	-71.0	-51.0
S 147	ϵ-caprolactone polyester (MW 2000)	MOCA/TMP	26.1	3.1	535	87	+36.0	+ 19.0	-35.0	- 1.0	+ 28.0	+ 58.0	+93.0	+ 7.0	Disintegrated				-66.0	+ 6.0	-42.0	- 5.0
S 148		MOCA	37.3	4.1	605	93	+ 8.0	+ 41.0	-31.0	0	-	-	-	-	Disintegrated				-54.0	+20.0	-36.0	- 1.0
S 151		TMP	9.3	1.7	420	73	+42.0	+ 41.0	-33.0	- 4.0	-	-	-	-	Disintegrated				-70.0	+47.0	-70.0	- 4.0
S 155	ϵ-caprolactone polyester (MW 500)	BD/TMP	40.7	7.1	310	82	+ 3.0	+135.0	-32.0	+21.0	+ 40.0	+ 96.0	+ 6.0	+18.0	-97.0	-94.0	+ 3.0	-65.0	-65.0	-54.0	-18.0	- 9.0
S 154		MOCA/TMP	42.2	6.3	335	85	-	-	-	-	-	-	-	-	-98.0	-95.0	+ 1.0	-65.0	-	-	-	-
S 160	polyether (MW 2000)	MOCA/TMP	11.6	4.3	355	89	+52.0	+ 21.0	- 7.0	- 3.0	+133.0	- 9.0	+79.0	- 3.0	+40.0	-49.0	+69.0	- 9.0	-31.0	+23.0	-49.0	-11.0
S 161		MOCA	29.4	6.2	505	95	- 7.0	+ 1.0	-18.0	- 1.0	- 3.0	- 10.0	+50.0	- 1.0	-87.0	-47.0	-37.0	- 9.0	-61.0	+ 8.0	-50.0	- 9.0
S 165		hydroxy propyl aniline	6.1	1.0	875	30	-48.0	- 20.0	+11.0	0	-	-	-	-	-	-	-	-	-77.0	-70.0	-20.0	0
S 173	polyether (MW 1000)	TMP	14.1	4.6	180	82	- 7.0	-	-47.0	+ 9.0	+134.0	+176.0	- 3.0	+ 6.0	-29.0	- 4.0	-17.0	- 4.0	-66.0	-	-53.0	- 2.0
S 175		BD	16.1	3.9	345	86	+83.0	+ 67.0	-29.0	- 5.0	-	-	-	-	-17.0	+13.0	-12.0	- 3.0	-55.0	+ 8.0	-48.0	- 9.0

Key:
MW = average molecular weight (nominal)
TS = tensile strength at break
M100 = modulus at 100 per cent extension
EB = percentage extension at break
H = hardness

MOCA = methylene bis-(2-chloroaniline)
TMP = 1,1',1"-trimethylol propane
BD = 1,4-butane diol
\- = not tested or value not recorded

4 3 Effect of Additives on the Properties of Polyurethane Elastomers

In an attempt to improve certain of the known shortcomings of some of the elastomer types described in Sections 4 1 and 4 2, for example resistance to photo-oxidation, the effects that various additives and/or stabilisers had on the ageing properties of the elastomers were assessed. The methods of preparation, basic formulations and testing procedures were identical with those described in Sections 2 and 3.

Details of the additives used, the initial mechanical properties of the elastomers and percentage changes in their original mechanical properties after ageing are summarized in Table 4. The properties of the modified elastomers and their comparison to the unmodified controls are summarised below.

HTPB Elastomer S 141 contained 2½ per cent by weight of an oil soluble nigrosine dyestuff. The initial mechanical properties of the elastomer containing dyestuff were similar to those of the unmodified elastomer S 140. The elastomer containing nigrosine showed slightly better resistance to dry air at 80°C compared with the unmodified elastomer but stiffened rather more during exposure to ultraviolet radiation and was inferior to S 140 as regards resistance to STF at 65°C.

HTBB Elastomer S 142 contained 2½ per cent by weight of carbon black. The initial mechanical properties of the elastomer and its resistance to dry air at 80°C and ultraviolet radiation were inferior to the unmodified elastomer S 140.

HTPB Elastomer S 144 was a syntactic* foam prepared by introducing 10 per cent by weight of hollow glass spheres to unmodified elastomer S 140. The material was buoyant, showing fair initial mechanical properties with fairly good ageing characteristics as shown by changes in original mechanical properties after ageing in water and dry air at 80°C, and ultraviolet light. The resistance of the material to STF at 65°C however was poor.

HTPB Elastomer S 146 contained 15% carbon black. However, no evidence of any reinforcing action was observed. The carbon black filled elastomer possessed reasonable resistance to dry air and water at 80°C like the unfilled elastomer.

ϵ-Caprolactone polyester urethane S 149 contained 2½ per cent by weight of an oil soluble nigrosine dyestuff. The introduction of the dyestuff gave a reduction in strength of the unaged elastomer compared to the unmodified material and no marked improvement in the resistance of the elastomer to dry air and water at 80°C was achieved, although there appeared to be a slight improvement in the resistance of the elastomer to ultraviolet light and STF at 65°C.

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*Syntactic foam is a buoyant composite consisting of a hollow spherical filler in a polymer matrix. These materials have generally good compression behaviour.

ϵ-Caprolactone polyester urethane S 150 contained both an ultraviolet absorber and an antioxidant based on a mixture of butylated hydroxy toluene and dilauryl thiodipropionate, as recommended in Reference 11. The unaged elastomer showed good initial mechanical properties with rather better ageing properties of exposure to dry air at 80°C and ultraviolet light than was obtained with the unmodified elastomer S 147.

ϵ-Caprolactone polyester urethane S 156 containing $2\frac{1}{2}$% carbon black showed a reduction in initial mechanicalproperties compared with the unmodified material S 155. However S 156, stiffened rather less in both dry air at 80°C and ultraviolet radiation compared with the unmodified elastomer. No improvement in resistance of the elastomer to water or STF was achieved.

ϵ-Caprolactone polyester urethane S 158 contained the ultraviolet absorber and antioxidant pair used in elastomer S 150 and gave an elastomer with improved initial mechanical properties compared with the unmodified elastomer S 155. The additives appeared to have little effect on the already reasonably satisfactory ageing properties of the elastomer towards dry air and ultraviolet radiation.

Polyether urethane S 163 contained 2.5 per cent by weight carbon black and 0.6 per cent by weight of the antioxidant mixture described above but gave no improvement, either in initial mechanical properties or resistance to ageing, compared to the unmodified polyether elastomer S 160.

Polyether urethane S 164 contained 0.6% antioxidant together with 10 per cent by weight of zinc oxide which was added with the object of improving the photo-oxidative stability of unmodified polyether elastomer S 160. The presence of zinc oxide however led to a deterioration in the initial mechanical properties of the elastomer and to considerable stiffening of the elastomer during exposure to dry air at 80°C. The elastomer was relatively unaffected by exposure to ultraviolet radiation.

Polyether urethane S 167 was a chemical modification of S 160 where 50% of the backbone polyether polyol was replaced with a hydroxyl-terminated polysiloxane. This had the effect of softening the elastomer and considerably increasing its extension at break. The elastomer gave fair resistance to dry air at 80°C and STF at 65°C but was affected by contact with water.

Polyester urethane S 177 contained 2.5 per cent by weight of polycarbodiimide added with the object of improving the hydrolytic stability. The elastomer showed some deterioration in initial mechanical properties but its resistance to hydrolysis was improved slightly.

Polyester urethane S 178 contained 2.5 per cent polycarbodiimide and an ultraviolet stabilizer and an antioxidant mixture. This elastomer again showed some deterioration in its initial mechanical properties but showed good ageing properties in dry air at 80°C and ultraviolet radiation, and gave slightly better resistance to water at 80°C compared with the unmodified elastomer S 176.

TABLE 4

EFFECT OF ADDITIVES ON AGEING PROPERTIES OF POLYURETHANE ELASTOMERS

Code No	Elastomer type	Additive	Initial properties (unaged)				Percentage change of original mechanical property after ageing for															
							28 days dry air (80°C)				10 days ultraviolet				28 days water (80°C)				28 days STF (65°C)			
			TS MN/m²	M 100 MN/m²	EB (%)	H BS°	TS	M 100	EB	H	TS	M 100	EB	H	TS	M 100	EB	H	TS	M 100	EB	H
S 140	hydroxyl-terminated polybutadiene	Nil	16.7	12.4	175	97	- 3.6	-	-54.0	0	- 6.5	+11.2	-28.0	0	+12.0	+ 6.6	-23.0	0	-74.0	-	-66.0	-35.0
S 141		2½% oil soluble nigrosine (a)	16.0	12.4	215	98	- 3.1	+ 27.0	-47.0	0	+ 6.0	+17.0	-63.0	0	-	-	-	-	-86.0	-	-67.0	-45.0
S 142		2½% carbon black (b)	11.8	-	37	98	+66.0	-	-57.0	- 3.0	-46.0	-	-73.0	+ 1.0	-	-	-	-	-	-	-	-
S 144		10% hollow glass spheres (c)	9.2	8.9	115	97	+13.0	-	-35.0	- 1.0	+ 9.0	-	-26.0	+ 1.0	+17.0	-	-48.0	+ 1.0	-88.0	-	-26.0	-70.0
S 146		15% carbon black (b)	16.2	-	95	89	+16.0	-	-49.0	0	-	-	-	-	+ 6.9	-	-52.0	- 3.0	-	-	-	-
S 147	ϵ-caprolactone polyester (MW 2000)	Nil	26.1	3.1	535	87	+36.0	+ 19.0	-35.0	- 1.0	-26.0	+19.0	+43.0	- 2.0	Disintegrated				-66.0	+ 6.0	-42.0	- 5.0
S 149		2.5% oil soluble nigrosine (a)	15.4	2.7	510	85	+23.0	+ 19.0	-30.0	- 5.0	+36.0	+11.0	-22.0	- 2.0	Disintegrated				-55.0	+20.0	-36.0	- 1.0
S 150		0.3% UV absorber (d), 0.6% antioxidant (f)	31.4	2.8	560	85	+ 2.0	+ 32.0	-36.0	- 1.0	-15.0	+25.0	-32.0	- 1.0	Disintegrated				-	-	-	-
S 155	ϵ-caprolactone polyester (MW 500)	Nil	40.7	7.1	310	82	+ 3.0	+135.0	-32.0	+21.0	+ 7.0	+82.0	-21.0	0	-97.0	-94.0	+ 3.0	-66.0	-65.0	-54.0	-18.0	- 9.0
S 156		2.5% carbon black (b)	24.6	8.1	285	78	+ 6.0	+ 98.0	-39.0	+21.0	- 6.0	+22.0	-33.0	+ 1.0	-97.0	-98.0	+33.0	-62.0	-76.0	-81.0	-32.0	- 4.0
S 158		0.3% UV absorber (g), 0.6% antioxidant (f)	37.8	6.7	325	80	+22.0	+163.0	-34.0	+24.0	+ 8.0	+72.0	-26.0	+ 1.0	-	-	-	-	-	-	-	-
S 160	polyether (MW 2000)	Nil	11.6	4.3	355	89	+52.0	+ 21.0	- 7.0	- 3.0	- 3.0	+16.0	-47.0	- 2.0	+40.0	-49.0	+69.0	- 9.0	-31.0	+23.0	-49.0	-11.0
S 163		2.5% carbon black (b), 0.6% antioxidant (f)	12.1	2.5	490	76	-68.0	- 40.0	-45.0	+ 4.0	-60.0	+36.0	-67.0	+ 4.0	-61.0	-48.0	-15.0	-41.0	-74.0	-29.0	-80.0	-26.0
S 164		10.0% zinc oxide, 0.6% antioxidant (f)	4.6	2.2	345	78	+89.0	+ 27.0	+ 3.0	- 3.0	- 9.0	+14.0	-38.0	- 5.0	-	-	-	-	-	-	-	-
S 167		50% polyether replaced with silicone polyol (h)	8.8	1.5	840	67	+23.0	+ 73.0	-38.0	0	-	-	-	-	0	-	-61.0	-33.0	-13.0	+27.0	-47.0	- 3.0
S 176	polyester (MW 2000)	Nil	32.2	3.6	555	88	+32.0	+ 28.0	-24.0	- 2.0	+ 2.0	+31.0	-32.0	+ 1.0	Disintegrated				-20.0	+ 6.0	-30.0	- 1.0
S 177		2.5% polycarbodiimide (i)	26.7	2.5	570	88	- 9.0	- 4.0	-17.0	-16.0	-	-	-	-	-70.0	-16.0	- 5.0	- 6.0	-29.0	0	-25.0	-17.0
S 178		2.5% polycarbodiimide (i), 0.12% UV absorber (j), 0.6% antioxidant (f)	23.5	2.7	545	87	- 2.0	+ 11.0	-25.0	0	- 1.0	+33.0	-35.0	- 1.0	-85.0	+19.0	-81.0	+10.0	-	-	-	-

MW = average molecular weight (nominal)
(a) Oil Soluble Nigrosine ex-ICI Dyestuffs Div
(b) Carbon black Vulcan 3F ex-Cabot Chemical Co
(c) Armospheres ex-JBC Plastics

(d) Tinuvin 320 ex-Giegy
(f) Irganox 1076 0.1% butylated hydroxy toluene ex-Geigy
Advastab 0.5% dilauryl thiodipropionate ex-Geigy
(g) Tinopol PGP ex-Geigy

(h) Silicone XR 6188 intermediate ex-Dow Corning
(i) Stabaxol DCD ex-Bayer
(j) Tinuvin P ex-Geigy

4 4 Low Temperature Flexibility

Table 5 compares the low temperature flexibility of five polyurethane elastomers described in the present work together with those of typical rubbers and two polyurethane elastomers examined previously.[10]

TABLE 5

Elastomer No	Type	T_{70}*, °C
S 140	hydroxyl-terminated polybutadiene/MDI/EHD	-40
S 147	ε-caprolactone polyester (MW 2000)/TDI/MOCA/TMP	-63
S 155	ε-caprolactone polyester (MW 500)/TDI/TMP/BD	+18
	polyether (MW 2000)/TDI/MOCA	-59
S 175	polyether (MW 1000)/MDI/BD	-85
S 176	ethylene/propylene adipate polyester/TDI/MOCA/TMP	+16
	propylene adipate polyester/TDI/hexane triol	-25
	natural rubber	-52
	nitrile	-25
	chloroprene	-37
	polysulphide	-46
	epichlorhydrin	-20
	acrylate	-10

*Temperature at which torsional modulus is 70 MN/m^2

Apart from polyester urethane elastomer S 176 which is highly crystalline and the low molecular weight caprolactone ester S 155, it will be seen that polyurethane elastomers are available possessing low temperature flexibility properties equal to or better than most conventional synthetic rubber elastomers.

4 5 Effect of Elastomer Thickness on Hydrolytic Stability

A limited investigation was made as to the effects of different film thicknesses on the original mechanical properties and hydrolytic stability of a polyurethane elastomer S 140 based on a hydroxyl-terminated polybutadiene which gave outstanding resistance to water previously.

The results are summarised in Table 6 below and in Figures 9 and 10.

TABLE 6

Range of values		Original properties (unaged)			Percentage changes in original mechanical properties after 28 days in water at 80°C		
Thickness (mm)	Cross sectional area (mm^2)	Tensile strength (MN/m^2)	100% modulus (MN/m^2)	Extension at break (%)	Tensile strength	100% modulus (MN/m^2)	Extension at break
0.86-0.91	3.50- 3.70	17.4	12.4	203	-6.3	+15.0	-39.0
1.12-1.17	3.70- 4.70	18.2	12.7	200	-1.5	+22.0	-35.0
2.15-2.23	8.70- 9.00	15.7	12.3	157	-4.5	+22.0	-41.0
2.71-2.82	11.10-11.30	16.0	11.7	182	-1.9	+25.0	-38.0
2.90-3.00	11.70-12.10	14.3	11.2	163	-0.7	+27.0	-40.0

Table 6 and Figures 9 - 10 suggest that there is a trend for tensile strength, 100 per cent modulus and extension at break to increase with decreasing film thickness, which is attributable to the fact that the number of mocroscopic flaws, occluded air bubbles etc present in a thin film will be less than those present in a thicker film.

After immersion in water for 28 days at 80°C, the thinner films appear to change rather more in strength than the thicker films. Losses of extension at break were similar but the thicker elastomers showed greater increases in 100 per cent modulus. Nevertheless over the range of thicknesses 0.86 - 3.00 mm the hydroxyl-terminated polybutadiene polyurethane elastomer showed very good resistance to hydrolysis.

5 CONCLUSIONS

A range of polyurethane elastomers have been prepared with satisfactory ageing properties when exposed to a wide variety of laboratory simulated environmental conditions. None of the elastomers gave satisfactory initial mechanical properties coupled with satisfactory resistance to all the selected conditions (Table 7) although certain polyether urethane elastomers prepared from polyoxybutylene glycols (average molecular weight 1000 - 2000) provided a reasonably acceptable compromise of properties under most conditions. These conditions included periods up to 28 days in dry air at 80 and 100°C, ultraviolet radiation, ASTM oil at 100°C, STF (petrol) at 65°C, water at 50, 80 and 100°C and retention of flexibility at low temperatures.

Hydroxyl-terminated polybutadiene/modified 4,4'-diphenyl methane di-isocyanate prepolymers crosslinked with 2-ethyl hexane 1,3-diol gave tough flexible elastomers with outstanding resistance to water at temperatures up to 100°C. The addition of hollow glass spheres to this elastomer produced a useful buoyant syntactic foam with satisfactory mechanical properties, coupled with good resistance to water.

The hydrolytic stability of the polyester urethanes, based either on caprolactone or adipate polyesters, was unsatisfactory, especially at temperatures above 50°C, although the caprolactone polyesters were rather better than the adipate polyesters in this respect. The addition of 2½ per cent polycarbodiimide to the polyester adipate urethane elastomer slightly improved its resistance to water. Adipate polyester urethanes showed rather better resistance to fuels compared to the caprolactone polyester urethanes.

The addition of ultraviolet absorbers and an antioxidant pair based on a mixture of butylated hydroxyl toluene and dilauryl thiodipropionate (see Table 7) appeared to give some improvement to the photo-oxidative/oxidative stabilities of the polyester urethane elastomers but this is difficult to substantiate by accelerated ageing trials. In this respect, most of the elastomers examined in the present investigation are also being exposed to natural weathering in temperate, hot/wet and hot/dry tropical environments; the results of these trials will be reported at a later date.

TABLE 7

PROPERTIES OF POLYURETHANE ELASTOMERS

Type of elastomer	Initial mechanical properties	Ageing properties after					Low temperature flexibility
		28 days dry air (80 - 100°C)	14 days ultraviolet radiation	9 days ASTM oil (100°C)	28 days STF (65°C)	10 - 28 days water (50 - 100°C)	
Hydroxyl-terminated polybutadiene	SATISFACTORY-GOOD Flexibility improves with 2-ethyl hexane 1,3-diol cure or use of TDI (see (2))	FAIR	SATISFACTORY	SATISFACTORY	POOR	GOOD	GOOD
ϵ-caprolactone polyester MW 2000	GOOD Strength improves by increasing % MOCA in cure	SATISFACTORY especially with BHT/DLTP antioxidant	SATISFACTORY especially with UV absorber and BHT/DLTP antioxidant	SATISFACTORY	POOR	SATISFACTORY <50°C POOR >50°C	GOOD
ϵ-caprolactone polyester MW 500	GOOD either with diol/triol or diamine/triol cure	SATISFACTORY	SATISFACTORY	SATISFACTORY	POOR	SATISFACTORY <50°C POOR >50°C	POOR
polyether MW 2000	FAIR-SATISFACTORY Strength improves by increasing % MOCA in cure	SATISFACTORY (up to 80°C)	SATISFACTORY	FAIR Improves with 100% MOCA cure	FAIR	SATISFACTORY with MOCA/TMP cure	GOOD
polyether MW 1000	SATISFACTORY Diol cure probably best - diamine too reactive	SATISFACTORY (up to 80°C)	SATISFACTORY	FAIR	POOR	SATISFACTORY	GOOD
ethylene/propylene adipate polyester MW 1000	GOOD	SATISFACTORY especially with BHT/DLTP antioxidant	SATISFACTORY especially with UV absorber	GOOD	GOOD	SATISFACTORY <50°C POOR >50°C Slight improvement with 2.5% polycarbodiimide	POOR

The addition of oil soluble nigrosine dyestuff appeared to be of some advantage in hydroxyl-terminated polybutadiene and caprolactone esters and was preferred to carbon black, since carbon black tended to reduce the initial tensile strength and provide less protection on ageing.

6 REFERENCES

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2	idem	ERDE Technical Report 39	23174 ✓
3	idem	ERDE Technical Report 53	26824 ✓
4	idem	ERDE Technical Report 54	26922 ✓
5	idem	ERDE Technical Report 68	28516 ✓
6		BS 903: Part A2: 1956	
7		BS 903: Part A7: 1957	
8		BS 2751: 1956	
9	Garvie W M, Gordon D	ERDE Report 9/R/64, p 5	✓
10	Brokenbrow B E, Sims D, Stokoe A L	ERDE Technical Report 40, p 3	23439
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12	Brokenbrow B E, Sims D, Wright J	Rubb J, June/July/Aug 1971 Reprint	

GLOSSARY

BD	1,4-butane diol
BHT	butylated hydroxy toluene
DLTP	dilauryl thiodipropionate
MDI	modified 4,4'-diphenyl methane di-isocyanate
MOCA	methylene bis-(2-chloroaniline)
TDI	toluene di-isocyanate
TMP	1,1',1''-trimethylol propane
MW	average molecular weight, nominal

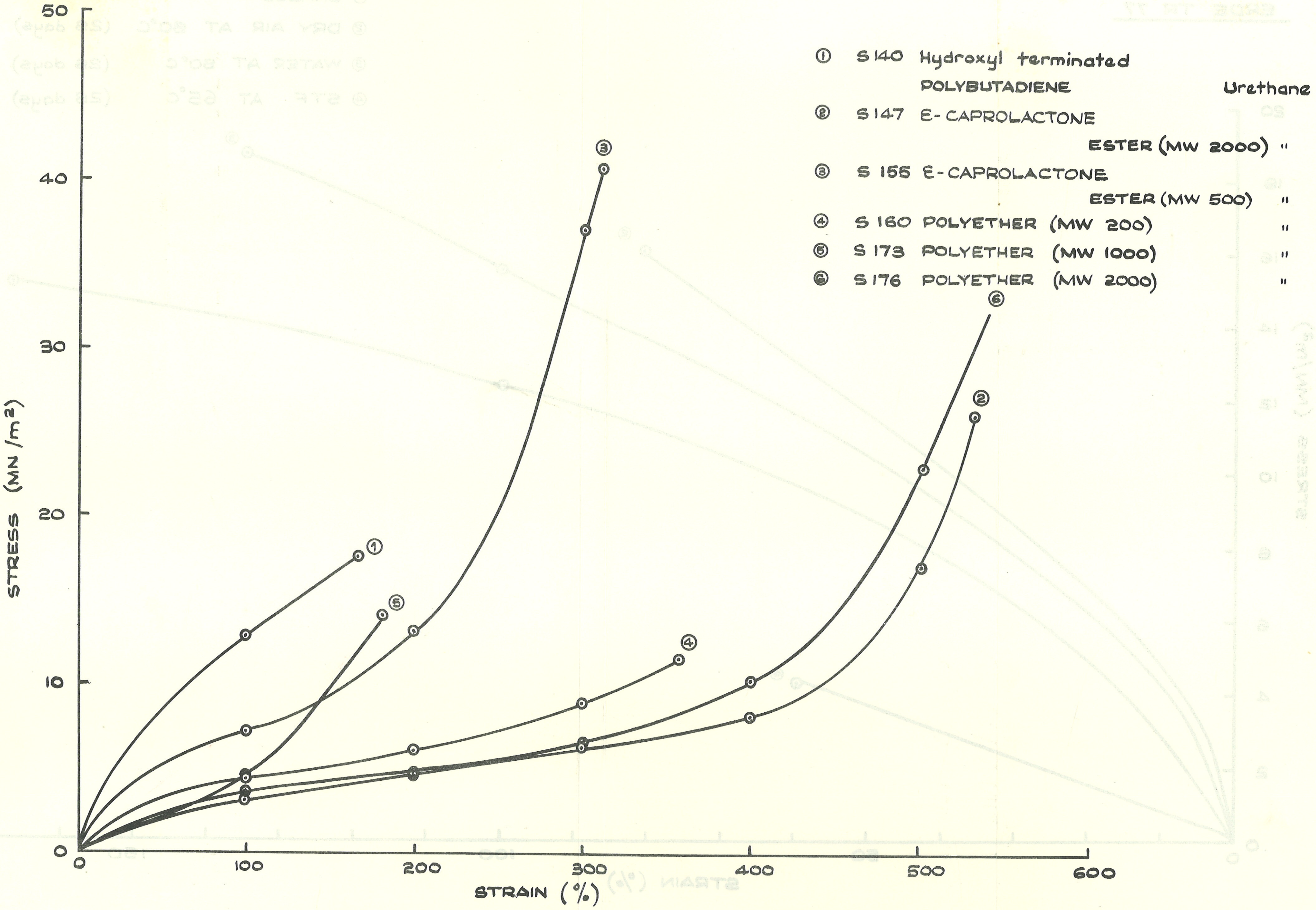


FIG. 1 STRESS/STRAIN CURVES OF SELECTED POLYURETHANE ELASTOMERS

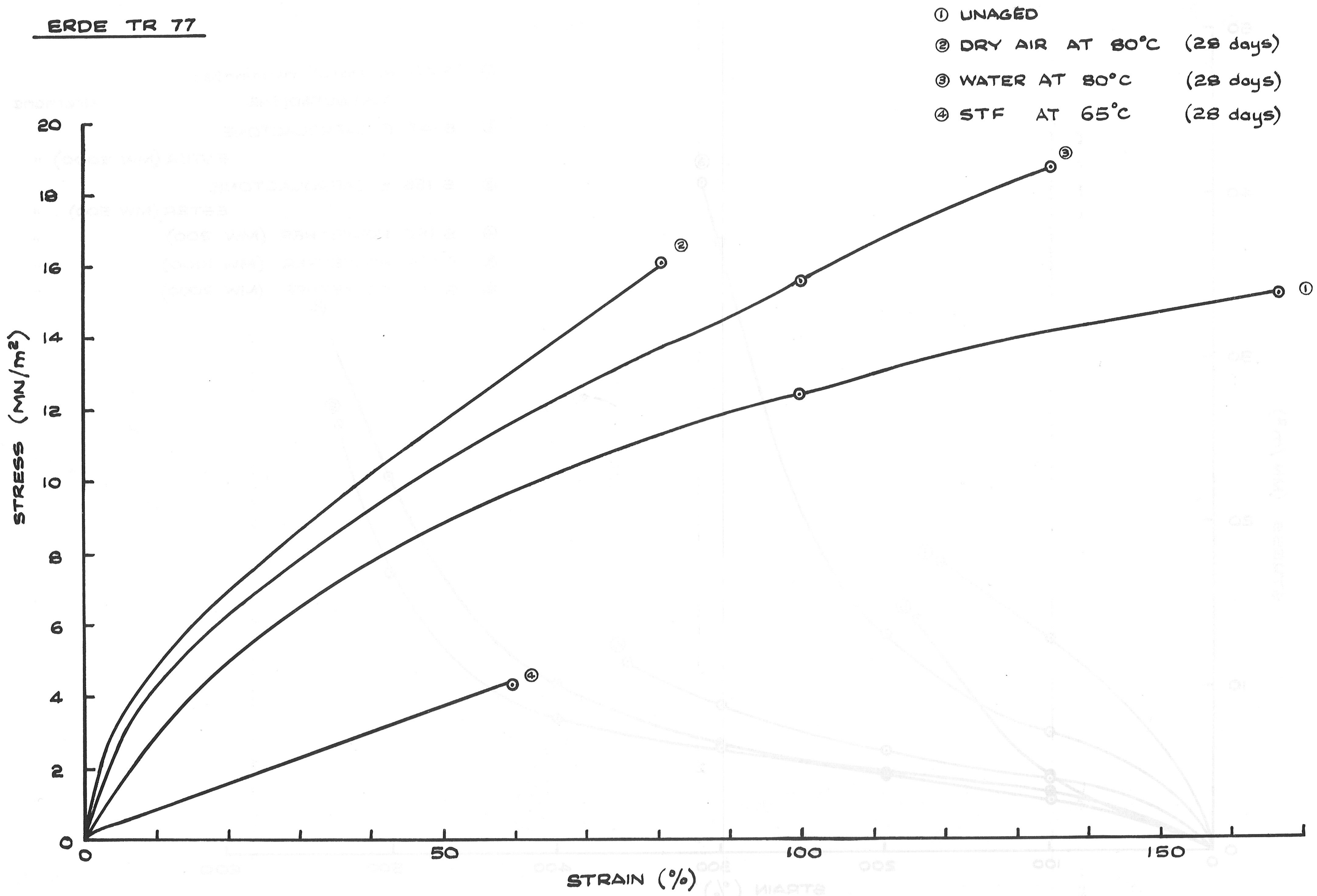


FIG. 2 EFFECT OF AGEING ON MECHANICAL PROPERTIES OF HYDROXYL TERMINATED POLYBUTADIENE URETHANE ELASTOMER (S 140)

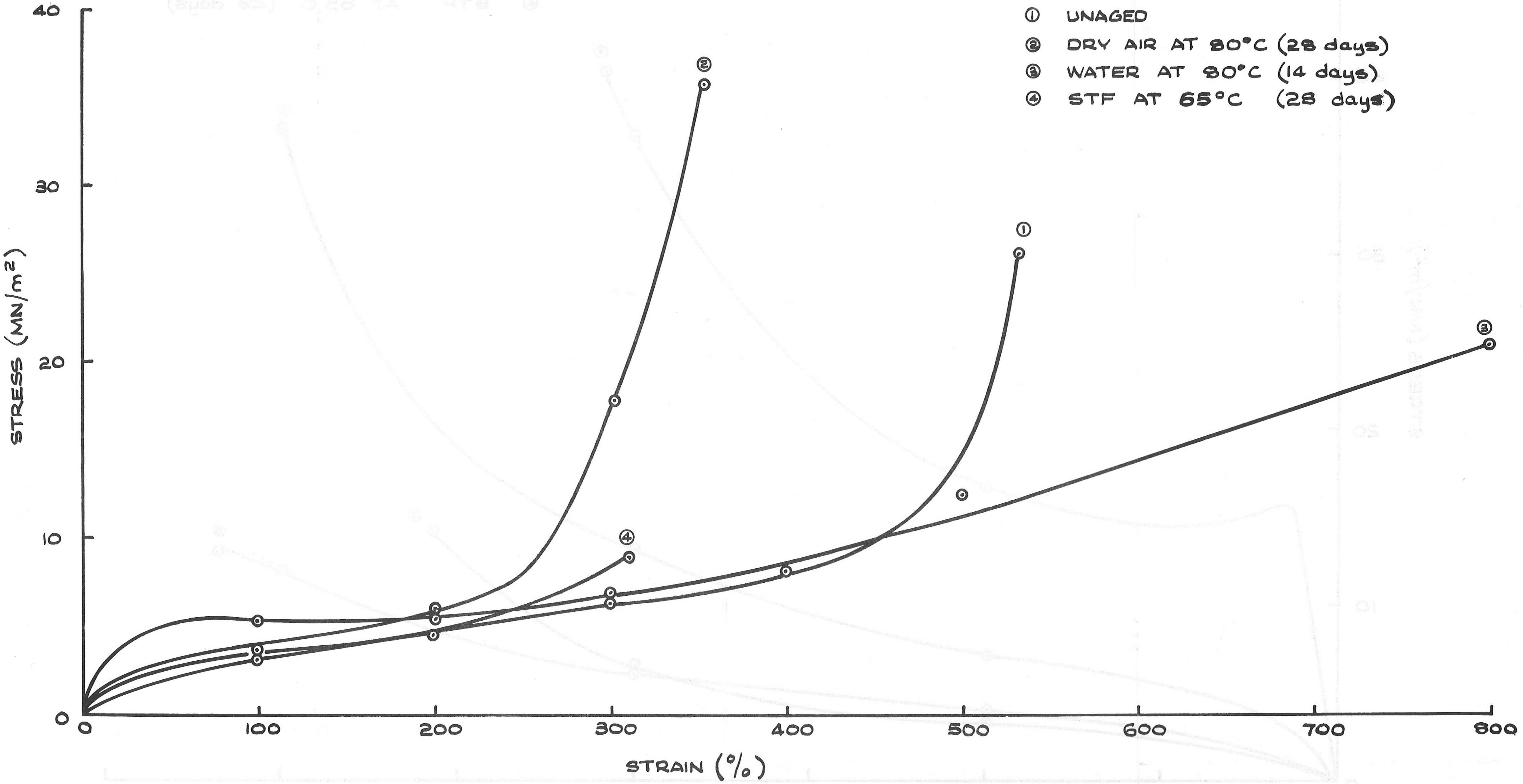


FIG. 3 EFFECT OF AGEING ON MECHANICAL PROPERTIES OF Є-CAPROLACTONE POLYESTER URETHANE (ESTER MW 2000) (S147)

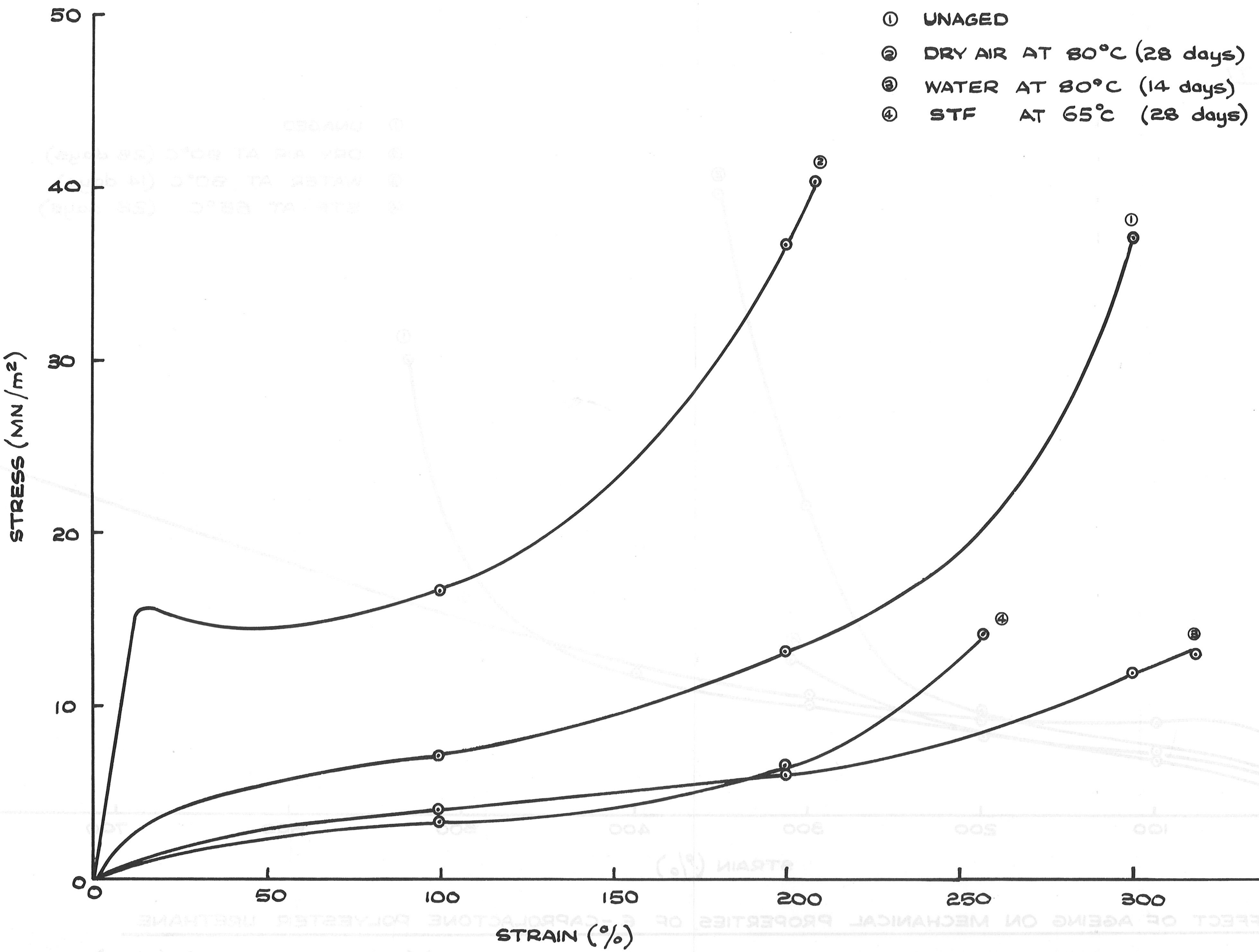


FIG. 4 EFFECT OF AGEING ON MECHANICAL PROPERTIES OF ε-CAPROLACTONE POLYESTER URETHANE

(ESTER MW 500) (S 155)

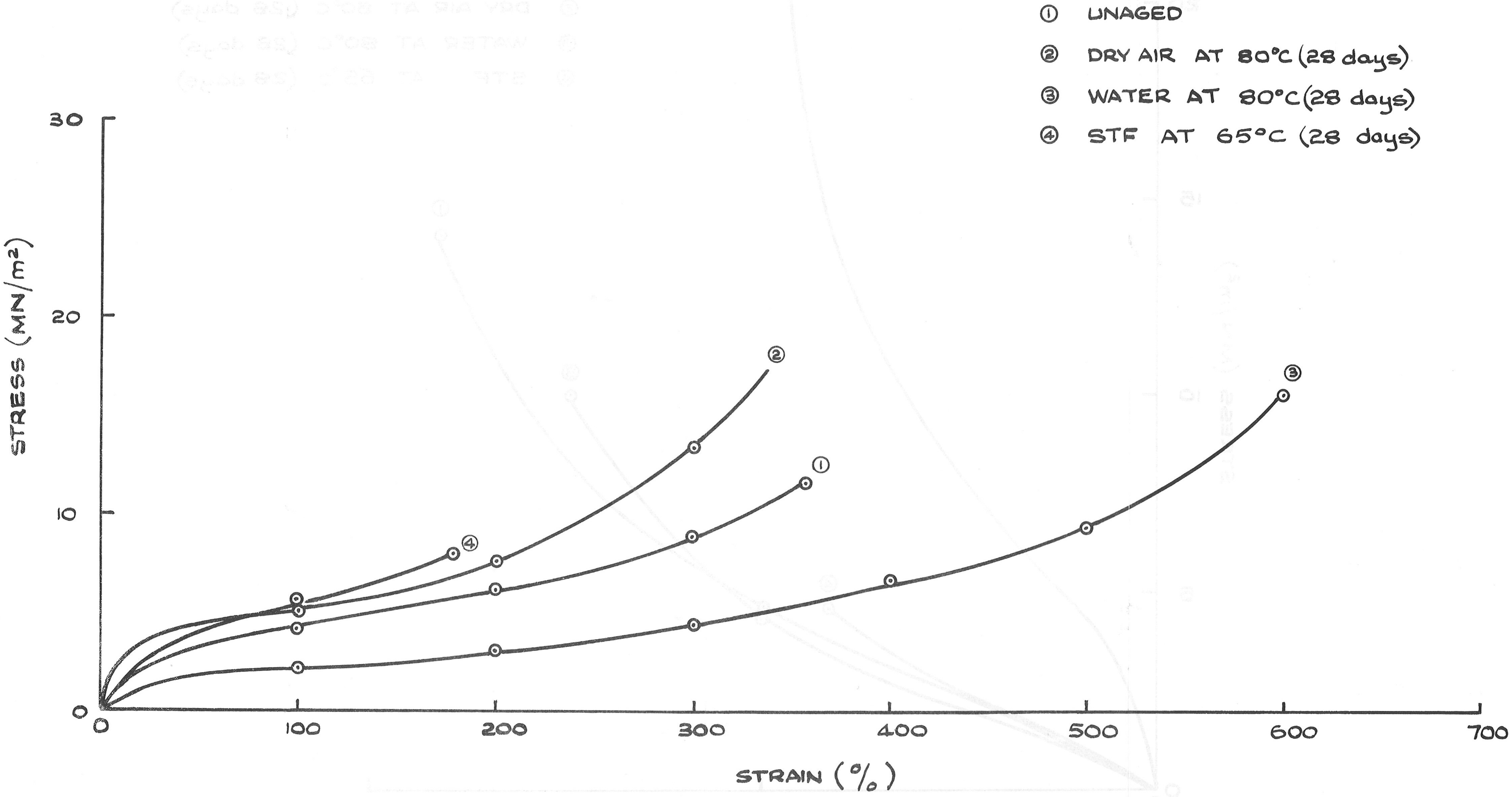


FIG. 5 EFFECT OF AGEING ON MECHANICAL PROPERTIES OF POLYETHER URETHANE (ETHER MW 2000) (S160)

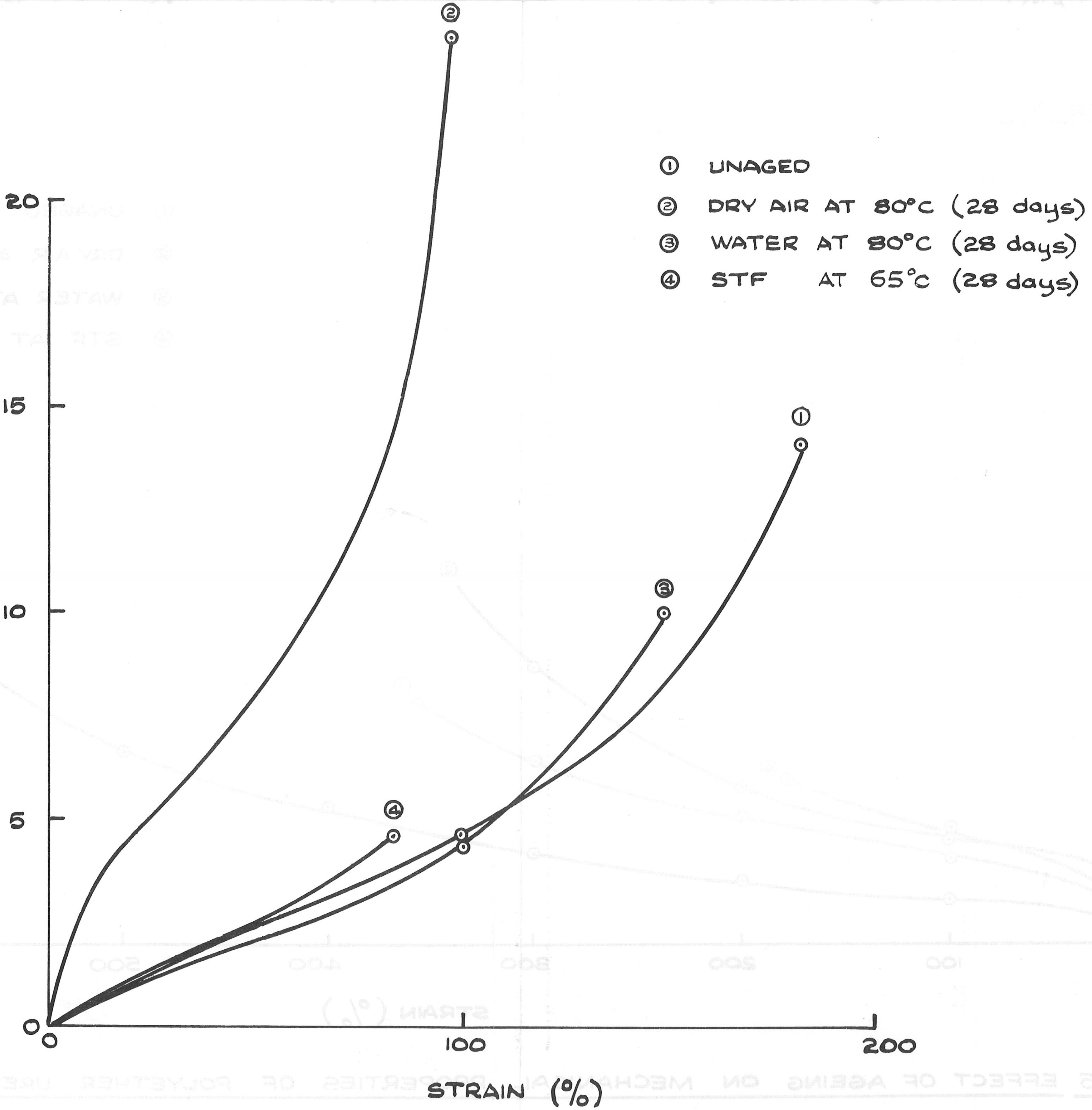


FIG 6. EFFECT OF AGEING ON MECHANICAL PROPERTIES OF POLYETHER URETHANE (ETHER MW 1000) (S 173)

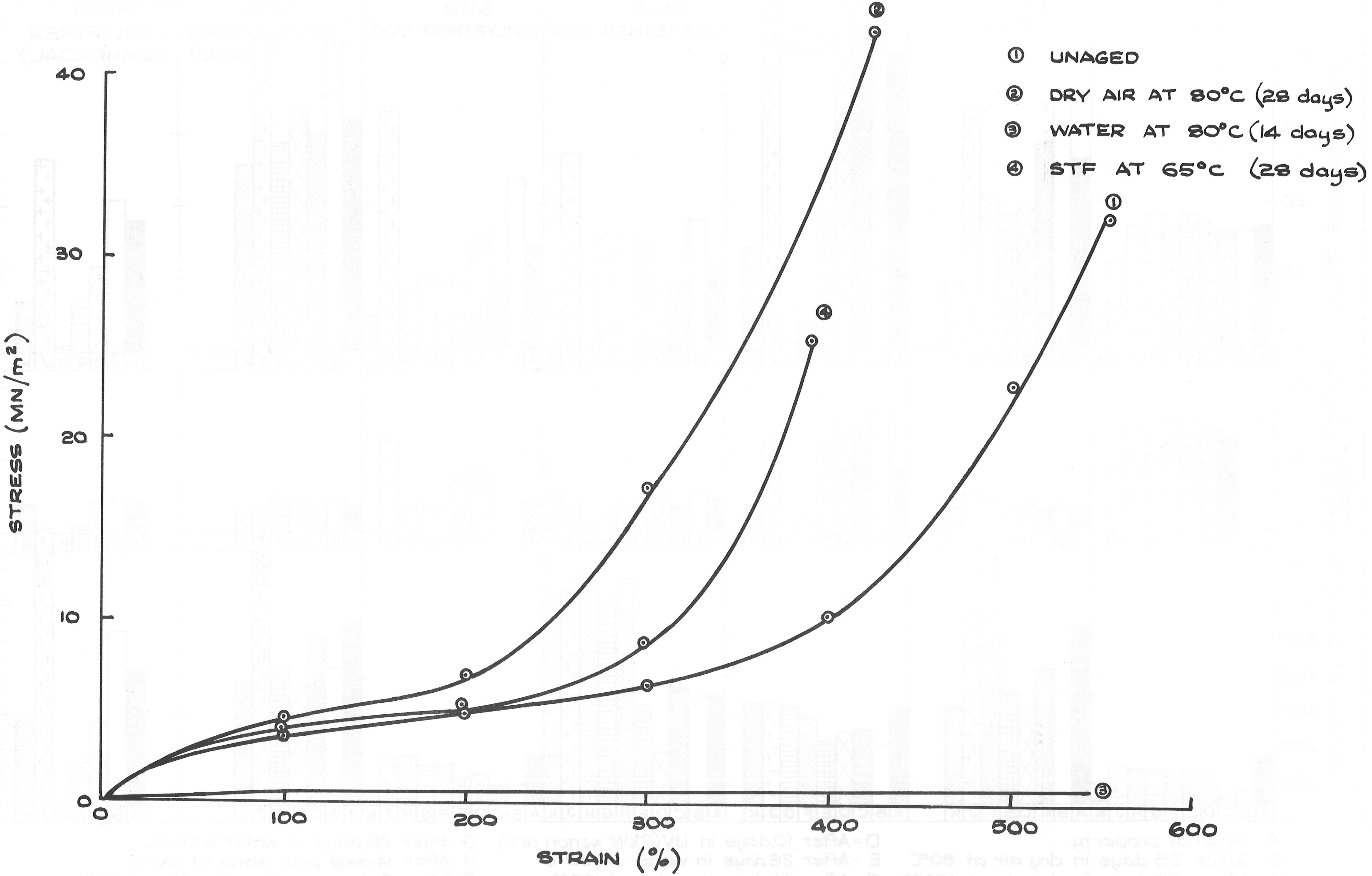
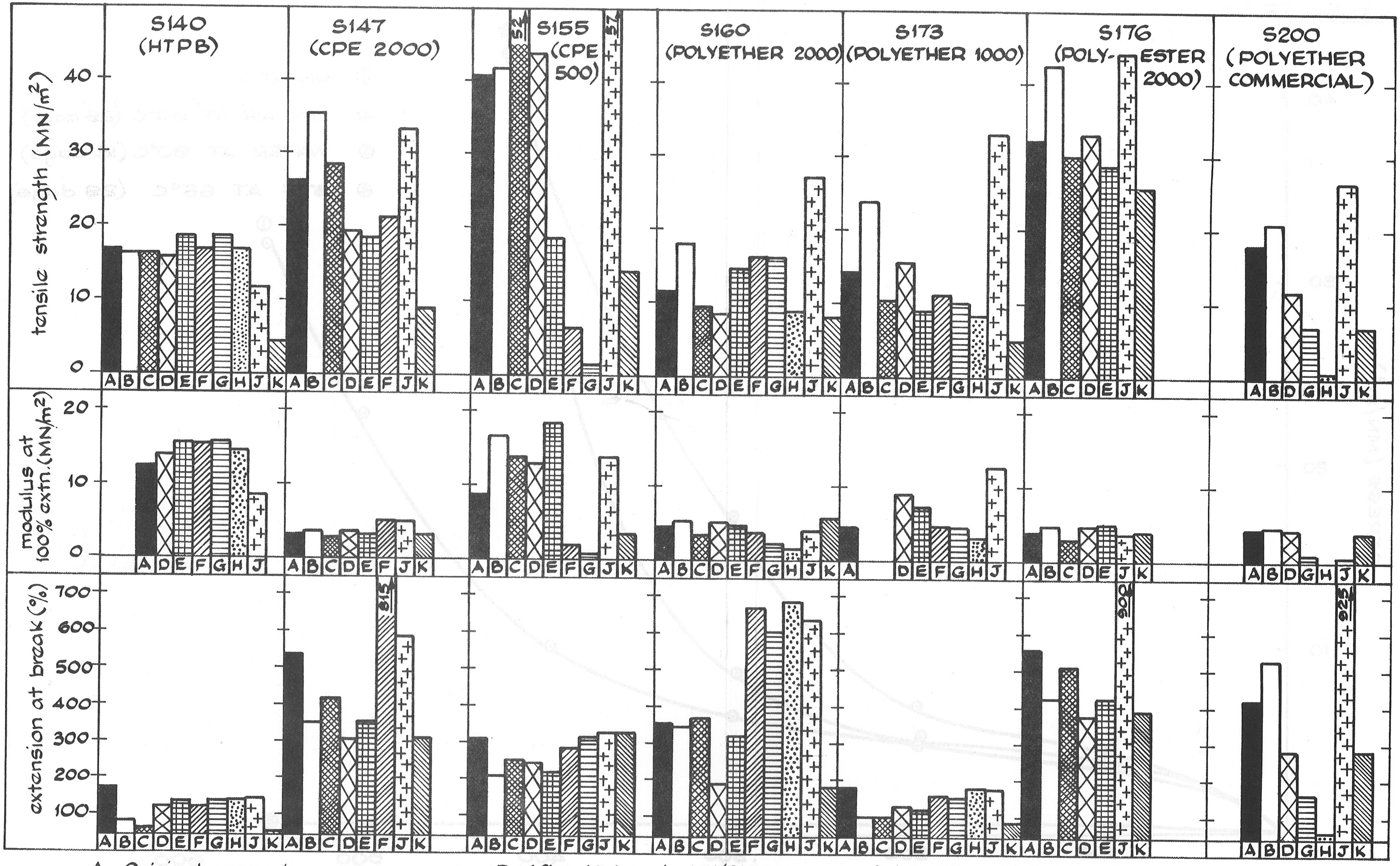


FIG. 7 EFFECT OF AGEING ON MECHANICAL PROPERTIES OF POLYESTER URETHANE (ESTER MW 2000) (S 176)



A = Original property
B = After 28 days in dry air at 80°C
C = After 28 days in dry air at 100°C
D = After 10 days in UV (2kW xenon arc)
E = After 28 days in water at 50°C
F = After 14 days in water at 80°C
G = After 28 days in water at 80°C
H = After 14 days over water at 100°C
J = After 9 days in ASTM oil Nº1 at 100°C
K = After 28 days in STF* at 65°C
*(STF = 70 : 30 v/v iso-octane : toluene)

HTPB = Hydroxy Terminated Polybutadiene
CPE = Caprolactone Polyester

FIG. 8 THE EFFECT OF AGEING IN ENVIRONMENTS ON TENSILE PROPERTIES OF POLYURETHANE RUBBERS

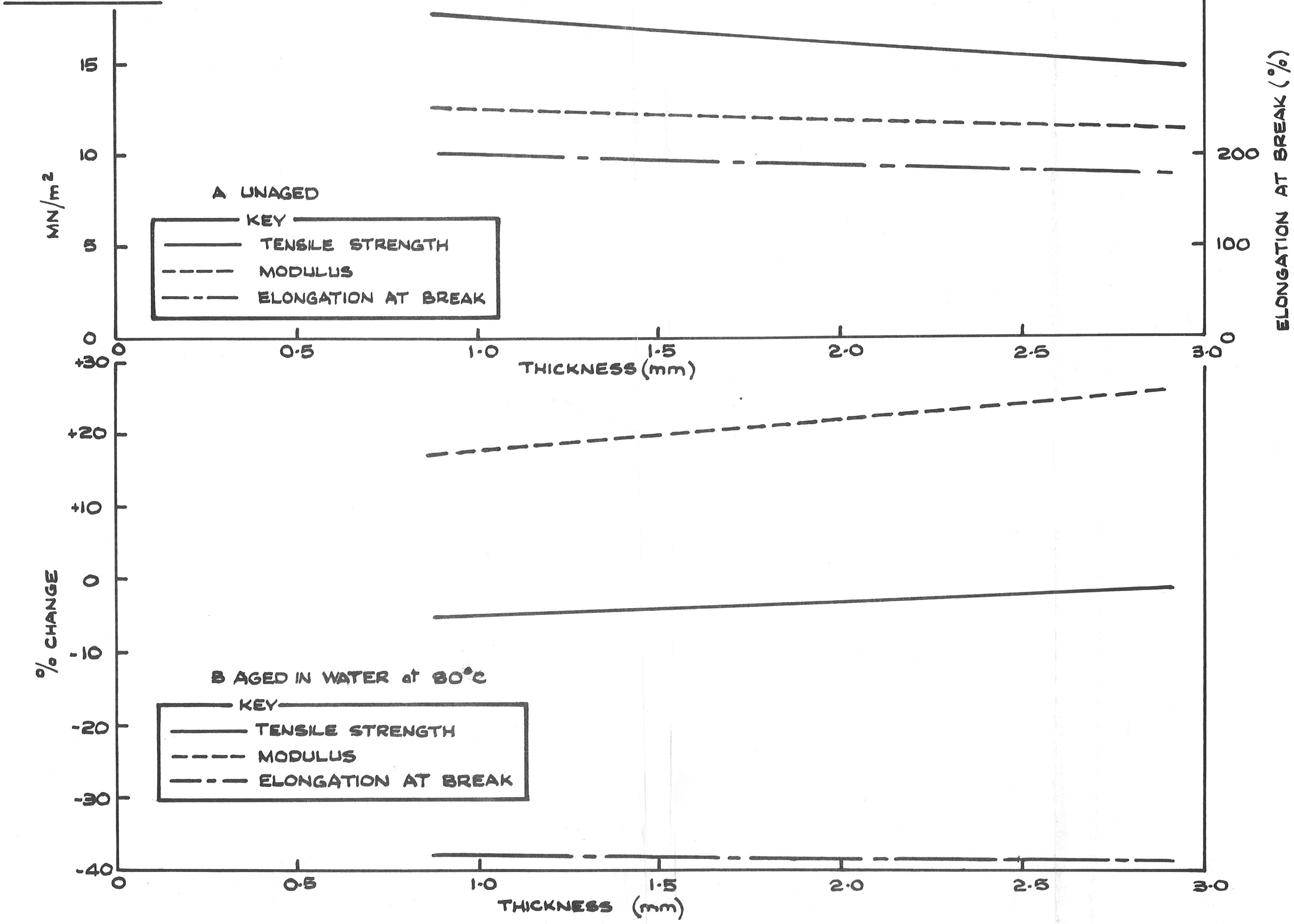


FIG. 9 EFFECT OF THICKNESS ON PHYSICAL PROPERTIES OF A POLYURETHANE

Technical Report No 77
Explosives Research and Development Establishment
HIGH PERFORMANCE POLYURETHANE ELASTOMERS: PART 1: LABORATORY AGEING TRIALS
Brokenbrow B E, Sims D, Wright J
January 1972
20 pp, 7 tabs, 9 figs

A range of polyurethane elastomers based on di-isocyanate prepolymers of polyether, hydroxyl-terminated polybutadiene, polyester adipate and caprolactone polyols have been prepared and their ageing properties assessed under a wide variety of laboratory simulated environmental conditions, including exposure to dry air (80 - 100°C), ultraviolet radiation; immersion in oil at 100°C, STF (65°C) and water (50 - 100°C).

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20 pp, 7 tabs, 9 figs

A range of polyurethane elastomers based on di-isocyanate prepolymers of polyether, hydroxyl-terminated polybutadiene, polyester adipate and caprolactone polyols have been prepared and their ageing properties assessed under a wide variety of laboratory simulated environmental conditions, including exposure to dry air (80 - 100°C), ultraviolet radiation; immersion in oil at 100°C, STF (65°C) and water (50 - 100°C).