J. nat Rubb. Res., **5(4)**, 266–274

Accelerated Long-term Ageing of Natural Rubber Vulcanisates Part 2: Results from Ageing Tests at 40°C

L. R. BARKER*

Studies of the influence of temperature on oven-ageing performance of black-filled natural rubber compounds vulcanised with conventional, semi-EV, EV and mixed Novor/sulphur curing systems have continued with testing at 40°C. With conventional and semi-EV vulcanisates, it was confirmed that the time to 80% retention of tensile strength followed an Arrhenius-type relationship but performance was above expectation for the EV compound. After five years at 40°C, tensile strength of the Novor/sulphur compound was still more than 80% of the unaged value as would be expected from ageing tests at higher temperatures. This compound also showed a tendency to increased modulus and longer fatigue life after ageing at 40°C as has been observed at higher ageing temperatures.

Studies of the influence of temperature on oven-ageing performance of black-filled natural rubber compounds vulcanised with conventional, semi-EV, EV and mixed Novor/sulphur curing systems were published in 1987 using results of tests carried out at 50°C–100°C on formulations given in *Table 1*[1].

It was found that the time to 80% retention of tensile strength during ageing followed an

TABLE 1. FORMULATIONS

Compound	Formulation			
	1	2	3	4
Natural rubber, SMR L	100	100	100	100
N330, HAF black	50	50	50	50
Aromatic process oil	4	4	4	4
Zinc oxide	5	5	5	5
Stearic acid	3	3	3	1
IPPD	2	2	2	–
TMQ	–	–	–	2
ZMBI	–	–	–	1
Sulphur	2.5	1.6	0.25	0.4
CBS	0.5	1.1	–	0.08
MBS	–	–	2.1	–
TMTD	–	–	1.0	–
TMTM	–	–	–	1.3
Novor 924[a]	–	–	–	4.2

[a]Urethane vulcanising agent (Rubber Consultants)

* Malaysian Rubber Producers' Research Association, Brickendonbury, Hertford SG13 8NL, United Kingdom (Retired)

Arrhenius-type relationship and changing the ageing temperature had the effect of altering relative resistance to degradation among the test compounds. Modulus changes during ageing were shown to be temperature-dependent and the earlier observations that, for a Novor curing system, ageing at 100°C gave a tendency to a higher tension fatigue life despite an increase in stiffness were confirmed for ageing at 50°C.

Concurrent with this work, but over a longer period, ageing tests at 40°C were also carried out on the same formulations. Apart from oven temperature, there were no changes in the experimental details already described[1].

The effect of ageing at 40°C on performance is of particular interest because this temperature is at the top end of a range that covers normal environmental conditions. Rubber would be expected to reach this temperature quite frequently in hotter parts of the world and in temperate regions, hot spots would be found indoors in areas such as near machinery and space heating systems where conditons are not severe enough to require special elastomers. A demonstration of the ability of accelerated ageing tests to forecast resistance to deterioration down to 40°C would therefore be of considerable practical value.

RESULTS

Effect of Temperature on Ageing

Table 2 is similar to Table 6 in the previous paper[1] but with data from ageing at 40°C incorporated. There are some small changes to Arrhenius slopes for *Formulations 1* and *2*, as would be expected, but the low probability levels indicate a considerable improvement in precision. A typical Arrhenius relationship is plotted in *Figure 1*.

It can be seen in *Table 3* that, for *Formulations 3* and *4*, tensile strength was not reduced enough by ageing at 40°C to estimate the time to 80% retention. This is understandable for the Novor/sulphur formulation because the estimate from earlier data indicated a time of nearly seven years but results are clearly above expectation for the EV compound.

With *Formulations 1* (15.5 min at 105°C), *2* (10 min at 150°C), *3* and *4* increases in tensile strength were observed after ageing eighty-seven weeks at 40°C. At higher temperatures, data were not obtained at sufficient short times to determine whether similar increases in tensile strength occurred. *Figures 2* and *3* relate to the performance of two compounds to ageing time at 40°C and 70°C. Time scales at the higher temperature have been adjusted according to the Arrhenius relationship using the following equation:

$$D_1/D_2 = \exp\,[B(10^3/T_1 - 10^3/T_2)] \qquad \ldots 1$$

where D_1 = ageing time at temperature T_1 (K)
D_2 = ageing time at temperature T_2 (K)
B = Arrhenius constant
= 10^{-3} × apparent activation energy/gas constant.

Effect of Ageing on Properties

Modulus and hardness. Even a casual examination of M100, M200 and hardness results indicates that, with a few exceptions, ageing at 40°C has generally increased stiffness over that at 50°C. This can be seen more clearly in *Figure 4* where percentage retentions of M100 for all the formulations are plotted against time of ageing at 40°C and 50°C with the time scales for the former temperature modified according to *Equation 1*. It can also be seen that increases in percentage retention are lower for the low sulphur formulations and for the shorter cure times with the conventional and semi-EV compounds relative to their overcures.

Compression set and resilience. Unstrained ageing of compression set test-pieces is probably not very informative for estimating performance in the deformed state but may be of some value for indicating the shelf-life of a component before being put into service. With three of the formulations, there were improvements in compression set after ageing at 40°C. Although ageing had less effect on the conventional compound when overcured, this did not compensate for the inferior unaged compression set.

TABLE 2. TIME OF AGEING TO 80% RETENTION OF TENSILE STRENGTH

Item	Formulation					
	1	2		3		4
Cure time, 150°C (min)	15.5	93	10	60	16	15
Experimental values (days)						
100°C	1.0	1.8	2.8	2.6	5.8	4.6
70°C	23	30	40	44	66	92
50°C	290	210	480	340	600	700
40°C	1 316	938	1 960	1 022	-	-
Regression estimates[a] (days, *versus* 1/T)						
100°C (days)	0.949	1.77	2.48	2.70	-	-
	(0.982)	(1.87)	(2.61)	(2.66)	(5.50)	(4.82)
40°C (years)	3.3	2.2	4.8	2.9	-	-
	(3.0)	(1.9)	(4.1)	(3.1)	(4.6)	(6.8)
Regression analysis Slope × 10^{-3}(B)	13.92	11.95	12.75	11.63	-	-
	(13.65)	(11.49)	(12.35)	(11.76)	(11.14)	(12.14)
Intercept	−37.4	−31.5	−33.3	−30.2	-	-
	(−36.6)	(−30.2)	(−32.1)	(−30.5)	(−28.2)	(−31.0)
Correlation coefficient	0.9997	0.9988	0.9985	0.9998	-	-
	(0.9999)	(0.9995)	(0.9985)	(0.9998)	(0.9990)	(0.9993)
	57.3	29.0	26.0	75.6	-	-
	(79.5)	(32.0)	(18.5)	(52.9)	(21.9)	(27.0)
Probability level (%)	0.03	0.12	0.15	0.02	-	-
	(0.8)	(2.0)	(3.4)	(1.2)	(2.9)	(2.4)

[a] Figures within brackets are estimated from results obtained at ageing temperatures 50°C, 70°C and 100°C only.

Increases in resilience observed for the EV compound are consistent with those found at higher ageing temperatures and probably indicate post-cure crosslink maturation. This effect should be minimised by vulcanising for a longer period. For the other formulations,

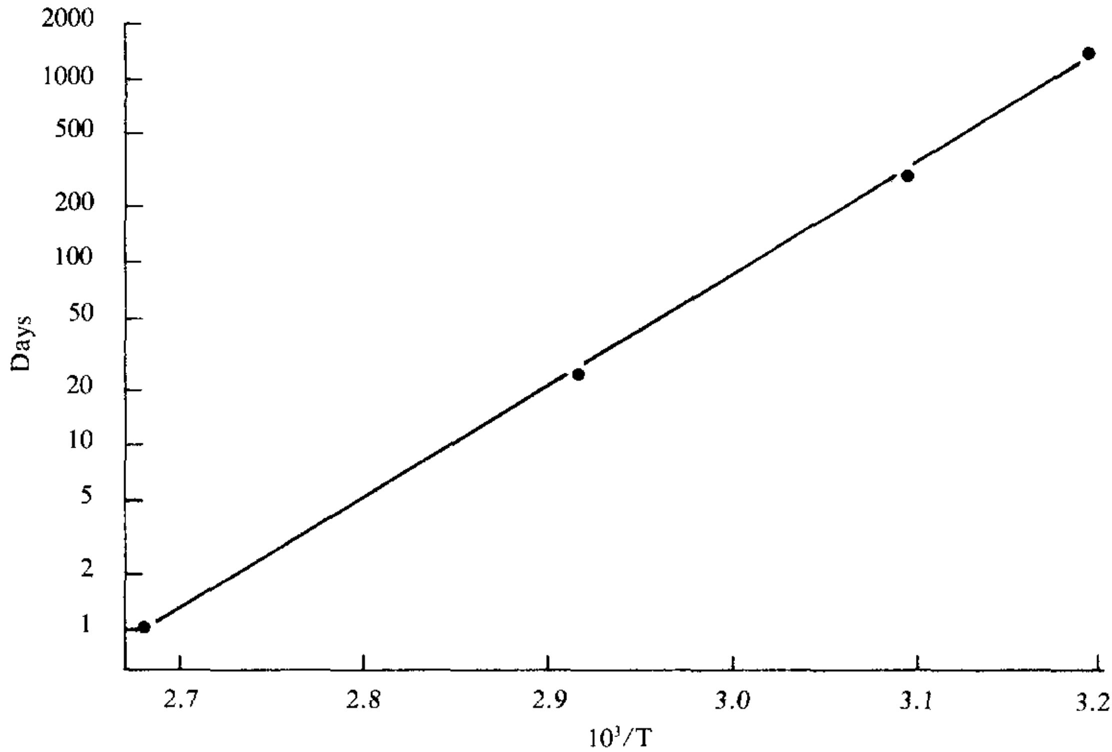

Figure 1. Arrhenius plot of ageing time to 80% retention of tensile strength, Formulation 1, cure 15.5 min at 150°C.

changes in resilience during ageing at 40°C were negligible.

Tension fatigue. Fatigue lives after ageing at 40°C might be expected to be lower than those at 50°C due to increased modulus but this is not evident in the results. Once again a positive change in fatigue performance was seen with the Novor/sulphur compound.

Ageing at 23°C. Over the period that ageing at 40°C was in progress, test-pieces were also stored at 23°C in the controlled atmosphere of a physical testing laboratory and results from these are included in *Table 3*. Storage time was equivalent to twenty to thirty-four weeks at 40°C and this mild severity of ageing is reflected in relatively lower changes in modulus and hardness. Further ageing at 23°C would be expected to lead to greater increases in stiffness. For similar reasons, changes in tensile strength and elongation at break were comparatively small with, in some instances, increases in values as seen with 40°C ageing.

High retention of fatigue life had the effect that conventional and semi-EV compounds still gave a better performance than those with EV or Novor/sulphur curing systems after five years at 23°C.

DISCUSSION

It is now well established that there are a number of chemical reactions that occur in rubber during ageing that lead to both molecular break-down and crosslinking. Each of these reactions proceeds at its own rate which is independently influenced by temperature. Results from these studies suggest that at high ageing temperatures network break-down leading to loss of strength tends to have the

TABLE 3. PERCENTAGE RETENTION OF PROPERTIES AFTER AGEING

Property	Formulation					
	1		2		3	4
Cure time, 150°C (min)	15.5	93	10	60	16	15
Ageing conditions						
M100						
40°C, 87 weeks	196	261	174	184	160	177
40°C, 174 weeks	267	282	186	214	163	166
40°C, 261 weeks	251	337	205	214	171	171
23°C, 261 weeks	174	155	122	139	130	140
M200						
40°C, 87 weeks	184	235	156	161	150	150
40°C, 174 weeks	212	232	154	172	145	140
40°C, 261 weeks	207	–	165	173	149	138
23°C, 261 weeks	154	136	111	123	120	122
Tensile strength						
40°C, 87 weeks	103	95	105	93	108	107
40°C, 174 weeks	84	69	86	75	95	93
40°C, 261 weeks	72	60	82	66	91	86
23°C, 261 weeks	105	91	95	97	107	102
Elongation at break						
40°C, 87 weeks	75	58	81	69	87	87
40°C, 174 weeks	57	43	74	45	85	76
40°C, 261 weeks	49	33	65	48	82	76
23°C, 261 weeks	95	84	94	92	104	98

TABLE 3. PERCENTAGE RETENTION OF PROPERTIES AFTER AGEING (Contd.)

Property	Formulation					
	1		2		3	4
Cure time, 150°C (min)	15.5	93	10	60	16	15
Ageing conditions						
Hardness						
40°C, 87 weeks	113	122	113	110	116	106
40°C, 174 weeks	116	127	115	116	113	105
40°C, 261 weeks	121	128	116	118	116	102
23°C, 261 weeks	109	114	109	106	104	101
Resilience						
40°C, 87 weeks	101	102	101	101	109	-
40°C, 174 weeks	98	99	101	97	111	102
40°C, 261 weeks	100	102	102	98	110	100
23°C, 261 weeks	95	98	100	98	105	105
Compression set						
40°C, 87 weeks	111	92	91	100	70	78
40°C, 174 weeks	111	100	82	109	70	83
40°C, 261 weeks	111	92	91	118	70	89
23°C, 261 weeks	100	108	100	127	90	89
Fatigue life						
40°C, 87 weeks	37	40	55	83	74	119
40°C, 174 weeks	15	5	30	23	69	110
40°C, 261 weeks	6	0	23	8	50	106
23°C, 261 weeks	85	81	75	98	90	80

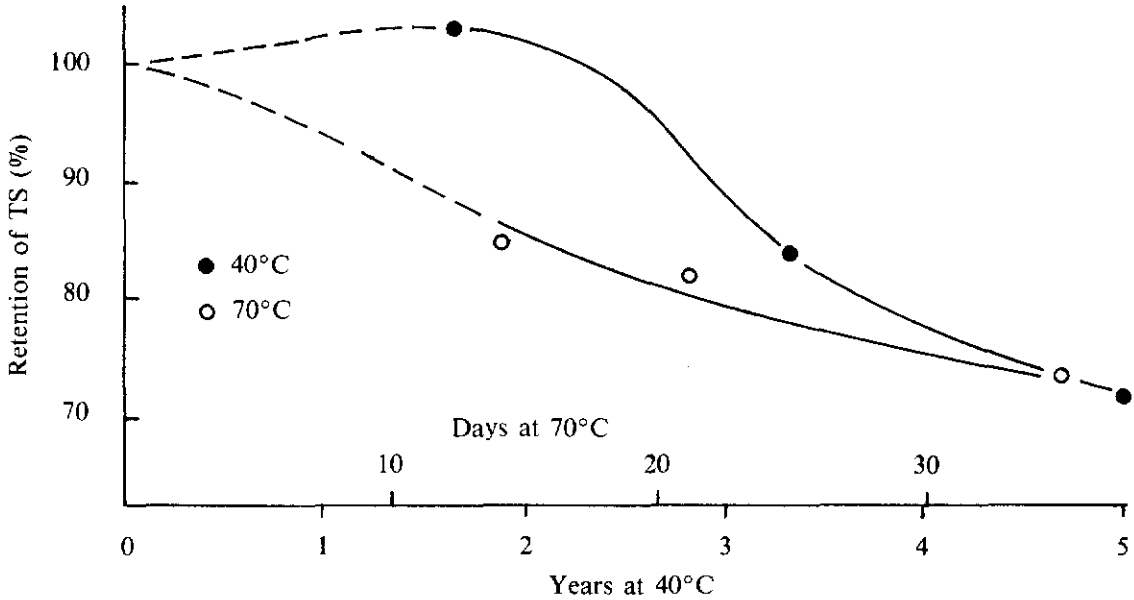

Figure 2. Percentage retention of tensile strength versus time of ageing at 40°C and 70°C, Formula 1, cure 15.5 min at 150°C.

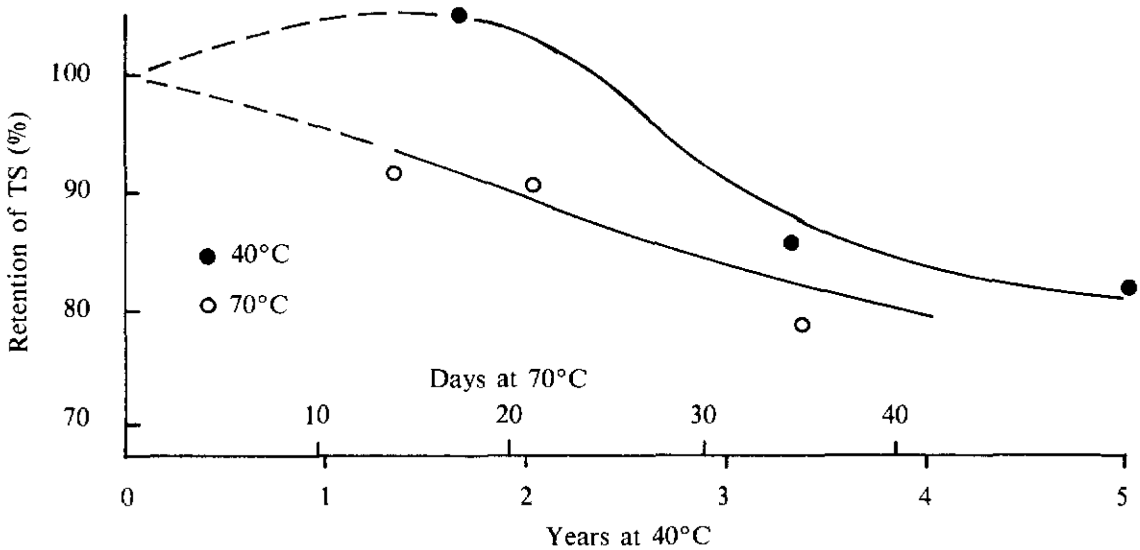

Figure 3. Percentage retention of tensile strength versus time of ageing at 40°C and 70°C, Formulation 2, cure 10 min at 150°C.

dominant influence while at lower temperatures crosslinking is relatively more important and can partly compensate for the effect of degradation. The difference in the net effect of these reactions at 40°C and 70°C can clearly be seen in *Figures 2* and *3* for conventional and

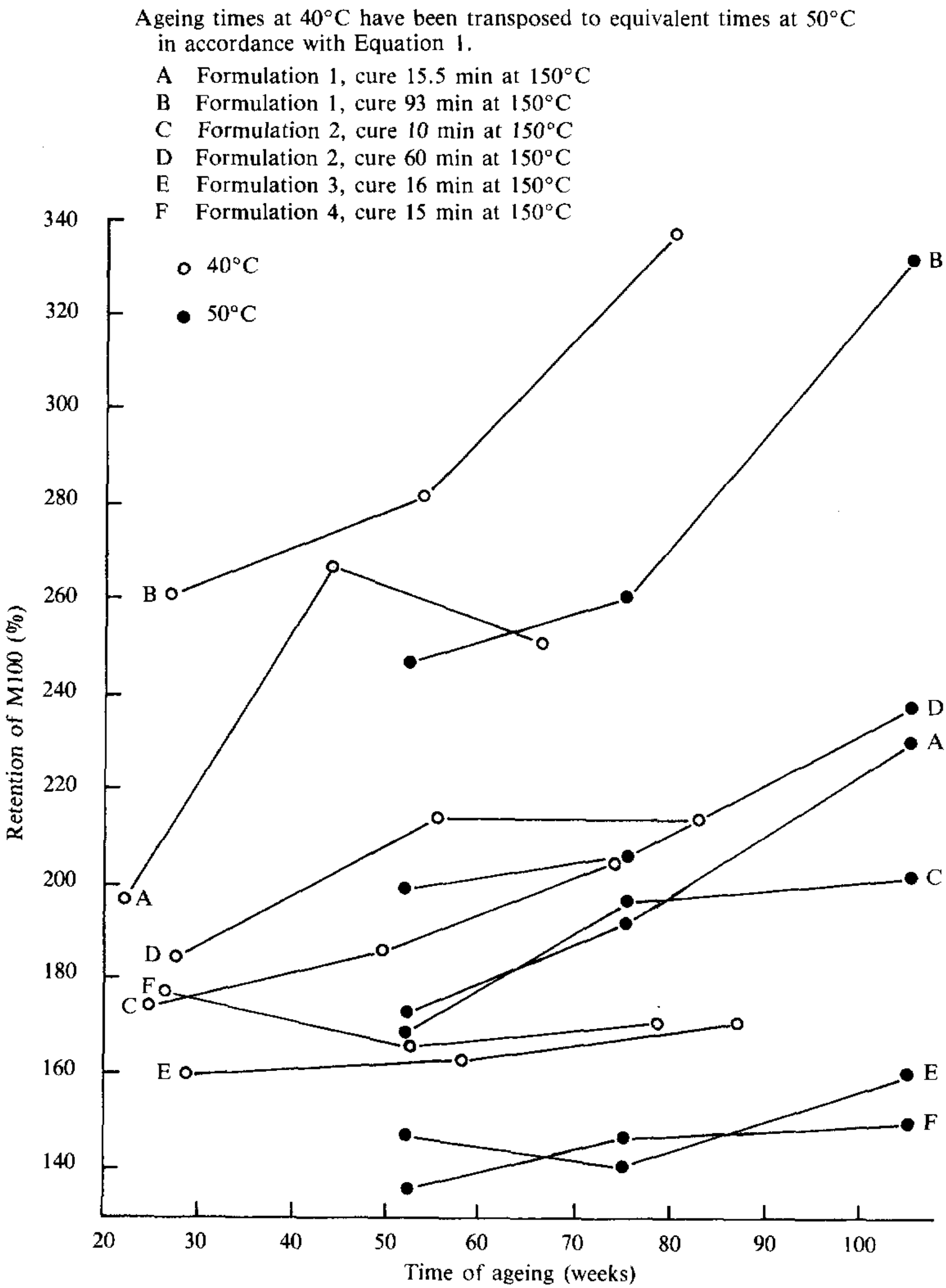

Figure 4. Retention of M100 versus time of ageing at 40°C and 50°C.

semi-EV curing systems and it is fortuitous that times to 80% retention of tensile strength at 40°C agree so well with predictions made from higher temperature results by the use of the Arrhenius expression. It seems likely that such predictions would break down for lower ageing temperatures as has happened at 40°C with the EV formulation.

CONCLUSIONS

Ageing tests at various temperatures have emphasised the complex nature of oxidative deterioration and the limitations of standard methods of assessment when the positive effects of crosslinking occur simultaneously with network degradation. With the conventional and semi-EV formulations used in this work, estimates of ageing by the Arrhenius method can be made with a reasonable degree of confidence down to 40°C but there is a risk of under-estimating ageing resistance at this temperature with the EV compound. Fortunately, this is a fail-safe situation: projections of ageing behaviour to below 40°C from results obtained at higher temperatures are likely to be pessimistic relative to performance in service.

ACKNOWLEDGEMENTS

The author would like to thank supporting staff at MRPRA for their practical involvement in this work and D.S. Campbell for helpful discussions relating to the interpretation of results. Thanks are also due to I.R. Gelling and A.J. Tinker for their advice during the preparation of this paper.

Date of receipt: June 1990
Date of acceptance: August 1990

REFERENCE

1. BARKER, L.R. (1987) Accelerated and Long-term Ageing of Natural Rubber Vulcanisates. *J. nat. Rubb. Res.*, **2(4)**, 201 [reprinted in *NR Technol., 1988*, **19(2)**, 28.]