JOURNAL OF MATERIALS SCIENCE **32** (1997) 3717–3725

Effect of 1,3-bis(citraconimidomethyl) benzene on the aerobic and anaerobic ageing of diene rubber vulcanizates

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The effect of 1,3-*bis*(citraconimidomethyl) benzene (Perkalink 900) has been investigated in diene rubber vulcanizates (truck-tyre tread-cap and tread-base compounds). Cure characteristics have been studied at 141 and 193 °C. Retention of physical properties after anaerobic (cured up to 2t90, 4t90 and 8t90) and aerobic ageing (aged for 1, 2, 3 and 4 weeks at 70 °C) has been found to be higher for the compounds with Perkalink 900. Heat build-up characteristics measured by Goodrich Flexometer and Martin's ball fatigue tester have been found to be lower for the Perkalink 900 compounds. Dynamic mechanical properties (tan δ) are reduced for the compounds containing Perkalink 900 even after extended cure. Fatigue to failure properties and abrasion resistance remain unaffected with the addition of Perkalink 900 in the compounds. The observed improvements in tyre-tread compound performance support the previously published mechanism of Perkalink 900.

1. Introduction

The phenomenon of reversion in sulphur-based cure systems, especially in natural rubber (NR) and polyisoprene rubber (IR) is well known in the rubber industry. Reversion occurs when polysulphidic cross-links are exposed to a temperature–time treatment which causes decomposition [1–3]. This phenomenon leads to a reduction in cross-link density and, consequently, loss of mechanical properties.

Reversion is not only a problem during curing, but it is also observed in rubber articles which are subjected to dynamic conditions during service, e.g. tyres. In the case of tyres, the heat generated during service can be sufficient to cause reversion. The reversion tends to be self-perpetuating, because it lowers the modulus which, in turn, accelerates the heat generation. Finally, the process leads to shortened service life or even premature failure. Many attempts, as for example the adoption of efficient vulcanization or sulphur donor cure systems, have been made to prevent or reduce reversion [4]. These vulcanization systems function by reducing the number of polysulphidic cross-links in the network whilst generating more mono- and disulphidic crosslinks. The improvement in reversion resistance is, however, achieved at the expense of flex and related strength properties. In addition, these compounds show poor rubber to metal and rubber to fabric adhesion due to faster cure rates and lower total sulphur levels. These limitations restrict the use of lower sulphur and sulphur donor cure systems in tyres.

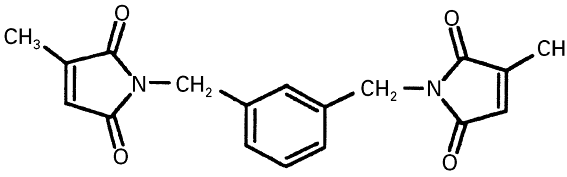
A rational solution to prevent reversion is to add an antireversion agent in the compound. Attempts along this line have been made by using various post-vulcanization stabilizers such as Duralink HTS, hexamethylene-1, 6-*bis* thiosulphate disodium dihydrate manufactured by Flexsys, America L.P. (formerly Monsanto Chemicals) [5] and Si-69, *bis*(3-triethoxysilyl propyl)-tetrasulphide manufactured by Degussa A. G., Germany [6–9]. Further, an investigation of zinc soaps of undisclosed composition has been reported [10]. However, each of these attempts suffers from some limitation and is far from an optimum solution [11].

The most recently developed antireversion agent is 1,3- *bis*(citraconimidomethyl) benzene (Perkalink 900), introduced by Akzo Nobel Chemicals b.v. (now Flexsys B.V.), Netherlands. This study is an endeavour to establish the antireversion characteristics of the newly developed material in current tyre-tread formulations.

2. Experimental procedure

2.1. Materials

The natural rubber used was RMA-4 procured from Kerala, India (ML1 + 4 at 100 °C = 79). The polybutadiene rubber used was CISAMER 1220 from I.P.C.L., Baroda (ML1 + 4 at 100 °C = 45). The antireversion agent, Perkalink 900 (I) was supplied by Flexsys b.v., Netherlands; other ingredients used were received from standard sources.



(I)

2.2. Mixing and processing

Formulations of the compounds used are given in Table I. Mixing of compounding ingredients with rubber was carried out in a laboratory Banbury of chamber volume 1.5 l. The mixing was done in two stages; in the first stage all ingredients except curatives and Perkalink 900 were added. The latter were added in the final stage of mixing. The dump temperature of the first stage was 160 °C, whereas for the final stage it was 100 °C. After mixing (both first and final stages) in the Banbury, the compound was subsequently passed five times through a two roll mill (33 cm × 15 cm). Compounds were then characterized for rheometric properties in MDR 2000E at 141 and 193 °C for 120 and 30 min, respectively. These were then cured at 141 °C up to different levels (t90, 2t90, 4t90 and 8t90) to prepare samples for mechanical and dynamic mechanical properties, where t90 is time for 90% cure; 2t90 is twice t90 and so on.

The different curing times were used to simulate the anaerobic ageing condition occurring in the inner parts of the tread of tyres during service. The percentage reversion was calculated by using the following equation [12, 13]

$$\text{Per cent reversion} = \frac{R_{\max} - R_{\max+t}}{R_{\max}} \times 100 \qquad (1)$$

where $R_{\max}$ is the maximum torque achieved and $R_{\max+t}$ is the torque measured after t min (here 15 min) beyond $R_{\max}$.

2.3. Testing

Stress–strain and tear properties of the vulcanizates were measured using a Zwick universal testing machine (model 1445) in accordance with ASTM D 412 and D 624 at a crosshead speed of 500 mm min^{-1}. Heat build-up was measured by a Goodrich Flexometer according to the method described in ASTM D 623. Heat build-up was also measured by using a Martin's ball fatigue tester at ambient temperature under 30 kg load and after 3250 revolutions.

Fatigue to failure properties were measured with a Monsanto fatigue to failure tester at an extension of 100%. Loss tangent, tan δ, of the vulcanizates was measured by a Dynamic Viscometer, Rheovibron model DDV-III. Hot-air ageing of various samples was done in a multicell ageing oven made by Tempo Instruments and Equipment (I) Pvt. Ltd, Bombay.

Abrasion loss of the tread-cap compounds was determined according to DIN-53416.

TABLE I Formulations

Ingredients[a] (p.h.r.)	Cap 1		Cap 2		Base	
	R[b]	E[c]	R[b]	E[c]	R[b]	E[c]
NR	100	100	50	50	100	100
BR	–	–	50	50	–	–
N330	52	52	60	60	–	–
N550	–	–	–	–	47	47
MBS	0.5	0.5	1.05	1.05	1.0	1.0
Sulphur	2.3	2.3	1.55	1.55	1.6	1.6

[a] Activator: ZnO–5 and Stearic acid–3 p.h.r. in all the formulations. Perkalink 900–1 p.h.r. in all the experimental compounds. NR, natural rubber; BR, polybutadiene rubber; MBS, benzothiazyl-2-sulphene morpholide.

[b] Reference compound.

[c] Experimental compound.

3. Results and discussion

3.1. Rheometric properties

The rheometric properties of cap 1, cap 2 and base compounds are shown in Figs 1–6 and reversion characteristics calculated from the rheographs by using Equation 1 are presented in Table II. It is clear from the figures that the control cap compounds show considerable reversion at both the test temperatures (141 and 193 °C). However, the experimental cap compounds, which contain 1 p.h.r. (parts per hundreds parts of rubber) of Perkalink 900, show negligible reversion. In the case

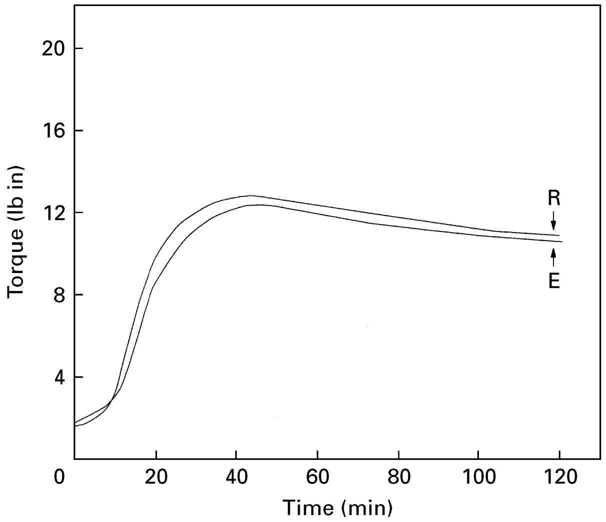


Figure 1 Cure characteristics of cap 1 compound at 141 °C. R, reference compound; E, experimental compound.

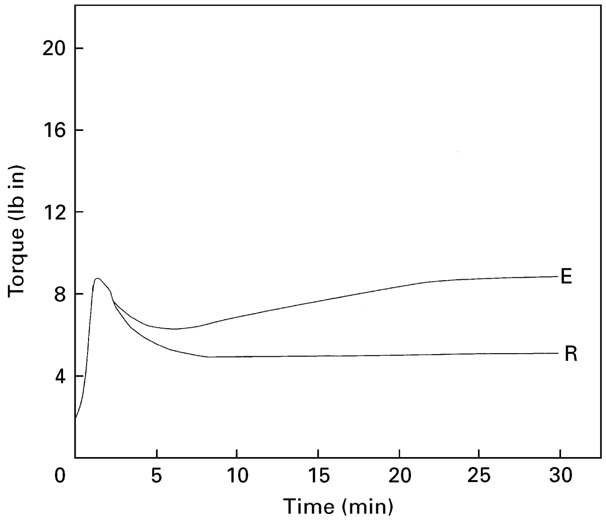


Figure 2 Cure characteristics of cap 1 compound at 193 °C.

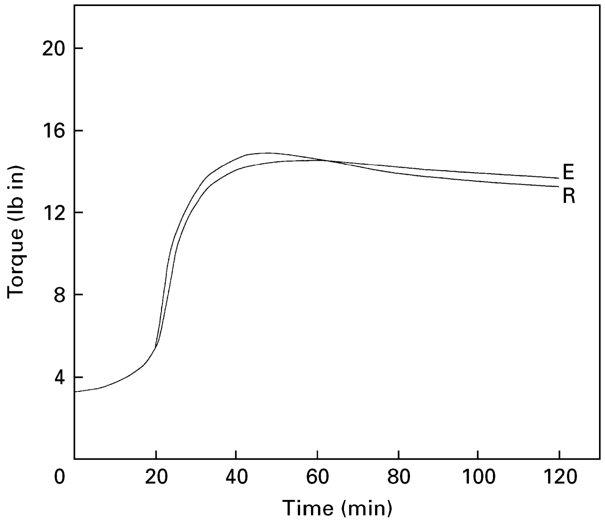


Figure 3 Cure chracteristics of cap 2 compound at 141 °C.

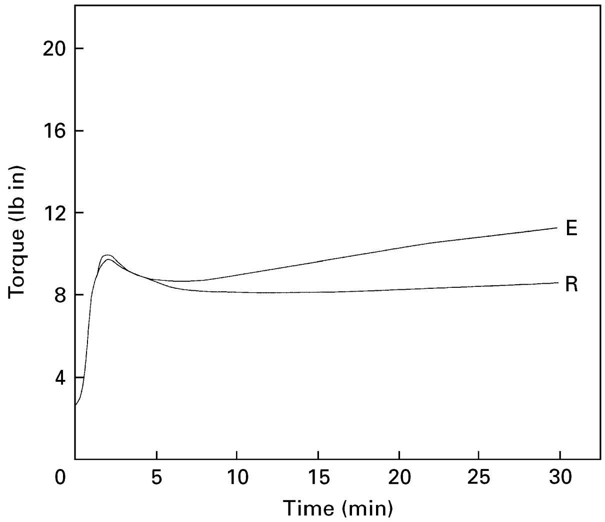


Figure 4 Cure characteristics of cap 2 compound at 193 °C.

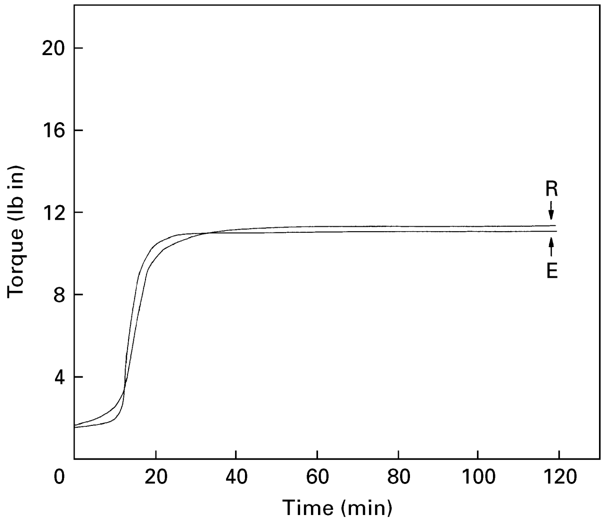


Figure 5 Cure characteristics of base compound at 141 °C.

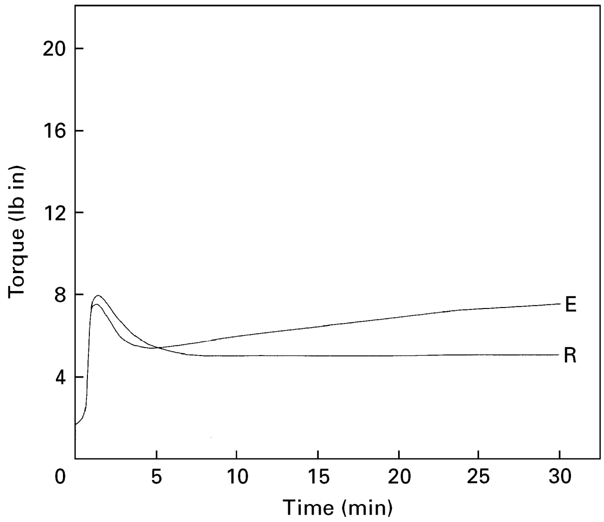


Figure 6 Cure characteristics of base compound at 193 °C.

TABLE II Reversion

Compounds	Type	Reversion (%)	
		141 °C	193 °C
Cap 1	R	11.4	43.4
	E	9.8	1.0
Cap 2	R	7.1	17.0
	E	4.4	0.8
Base	R	0	38.0
	E	0	12.0

of the base compound (featuring a semi-efficient vulcanization system), both the regular and experimental compounds show no reversion at 141 °C. However, considerable reversion (38%) was observed at 193 °C for the regular compound, but for the experimental compound (Table II) substantially less (12%). It is interesting to note that the presence of Perkalink 900 in the compounds does not change the cure characteristics.

3.2. Mechanical properties

Mechanical properties of the vulcanizates cured up to different levels, namely, t90, 2t90, 4t90 and 8t90, are tabulated in Table III. Vulcanizates cured up to t90 were aged for 1, 2, 3 and 4 weeks at 70 °C and the properties are given in Table IV. These processes are also known as anaerobic and aerobic ageing, respectively. The anaerobic ageing process simulates ageing during actual service of the inner portion of the tread, whereas aerobic ageing simulates it in the outer portion. It can be seen from Table III that the retention of properties such as modulus (at 100%, M100 and 300%, M300 elongation), tensile strength (TS), etc., are higher for the experimental compounds than the control compounds. The retention of modulus on overcure is a clear indication of compensation of reduced cross-link density that normally occurs during reversion.

When the vulcanizates of the cap and base compounds were aged under aerobic conditions, retention

TABLE III Physical properties (cured at different levels)

Cure time (min)	Properties	Cap 1		Cap 2		Base	
		R	E	R	E	R	E
t90	M100 (MPa)	2.8	2.8	2.0	2.0	2.4	2.1
	M300 (MPa)	10.8	10.8	7.1	7.2	9.4	8.3
	TS (MPa)	25.0	24.4	21.7	21.4	23.5	24.1
	EB (%)	545	535	630	630	550	590
	TR ($N mm^{-1}$)	112	118	87	79	48	51
2t90	M100 (MPa)	2.3	2.7	2.0	2.0	2.2	2.1
		(82)[a]	(96)	(100)	(100)	(92)	(100)
	M300 (MPa)	8.7	10.2	6.8	6.9	8.8	8.3
		(81)	(94)	(96)	(96)	(94)	(100)
	TS (MPa)	20.0	21.1	20.9	20.2	24.2	22.2
		(80)	(86)	(96)	(94)	(103)	(92)
	EB (%)	525	495	645	615	575	565
		(96)	(93)	(102)	(98)	(105)	(96)
	TR ($N mm^{-1}$)	94	96	87	92	44	46
		(84)	(81)	(100)	(116)	(92)	(90)
4t90	M100 (MPa)	2.1	3.0	1.8	2.0	1.9	2.1
		(75)	(107)	(90)	(100)	(79)	(100)
	M300 (MPa)	7.7	11.5	6.0	6.8	7.7	8.4
		(71)	(106)	(85)	(94)	(82)	(101)
	TS (MPa)	16.7	19.5	20.3	19.3	22.2	21.2
		(67)	(80)	(94)	(90)	(94)	(88)
	EB (%)	515	540	685	605	585	550
		(94)	(100)	(109)	(96)	(106)	(93)
	TR ($N mm^{-1}$)	27	37	80	79	44	43
		(24)	(31)	(92)	(100)	(92)	(84)
8t90	M100 (MPa)	2.1	2.9	1.7	2.4	2.0	2.2
		(75)	(104)	(85)	(120)	(83)	(105)
	M300 (MPa)	7.9	11.0	5.7	8.1	7.9	8.7
		(73)	(102)	(80)	(113)	(84)	(105)
	TS (MPa)	17.8	20.2	17.7	16.6	21.2	21.3
		(71)	(83)	(82)	(78)	(90)	(88)
	EB (%)	525	465	650	500	560	540
		(96)	(87)	(103)	(79)	(102)	(92)
	TR ($N mm^{-1}$)	25	42	77	74	42	39
		(22)	(36)	(89)	(94)	(88)	(76)

[a] Figures within the parentheses indicate per cent retention of the properties.

of modulus and tensile strength of the experimental compounds is higher than the regular in most of the cases (Table IV). This observation is quite prominent in the case of cap 2 compound. Tear resistance (TR) properties remain unaffected for the Perkalink 900-containing compounds.

It is well known that retention of physical properties such as modulus, tensile strength, etc., provides a measure of ageing resistance. The foregoing discussion reveals that the vulcanizates containing Perkalink 900 have higher retention of the properties in most of the cases. This suggests that Perkalink 900 cross-links [14], unlike sulphidic cross-links [15], are not only thermally stable but also resistant to oxidative degradation and hence are stable under the service conditions. The increase in modulus particularly of cap 1 vulcanizate, unlike the modulus increase for the control compound, will not negatively affect the dynamic properties, because the cross-links of Perkalink 900 are flexible and stable under the service conditions [16].

3.3. Heat build-up characteristics

When a tyre is in service, i.e. subjected to a cyclic strain, the rubber vulcanizate is not deformed in a purely elastic manner, but tends to dissipate some of the energy. Consequently, a portion of the motive power transmitted from the engine to drive wheels is absorbed due to the tyre hysteresis and thus transformed into heat. This heat generation leads to a rise in the tyre temperature and may ultimately lead to premature failure of the tyre. The reduction of heat generation is, therefore, an issue that compounders have addressed for years.

Heat build-up values of unaged vulcanizates of cap 1, cap 2 and base compounds are shown in Figs 7–9. It is clear from the figures that heat generation is considerably lower and tends to a constant value for the compounds containing Perkalink 900, compared to the control compounds (Figs 7 and 8). For the base compound, heat generation is comparable for both the regular and the compound containing Perkalink 900. A similar behaviour is observed when heat build-up values were measured even after ageing the samples

TABLE IV Physical properties (before and after aerobic ageing)

Ageing time (wk)	Properties	Cap 1		Cap 2		Base	
		R	E	R	E	R	E
Unaged	M100 (MPa)	2.8	2.8	2.0	2.0	2.4	2.1
	M300 (MPa)	10.8	10.8	7.1	7.2	9.4	8.3
	TS (MPa)	25.0	24.4	21.7	21.4	23.5	24.1
	EB (%)	545	535	630	630	550	590
	TR ($N mm^{-1}$)	112	118	87	79	48	51
1	M100 (MPa)	3.3	3.0	2.4	2.5	2.5	2.5
		(118)[a]	(107)	(120)	(125)	(104)	(119)
	M300 (MPa)	12.6	11.4	8.8	9.1	10.1	10.0
		(117)	(106)	(124)	(126)	(107)	(120)
	TS (MPa)	22.0	25.1	20.4	20.4	22.0	22.8
		(88)	(103)	(94)	(95)	(94)	(95)
	EB (%)	565	545	535	535	510	520
		(104)	(102)	(85)	(85)	(93)	(88)
	TR ($N mm^{-1}$)	90	113	88	98	42	41
		(80)	(96)	(101)	(124)	(88)	(80)
2	M100 (MPa)	3.4	4.7	3.2	3.8	2.9	3.0
		(121)	(168)	(160)	(190)	(121)	(143)
	M300 (MPa)	12.6	12.2	9.2	10.4	10.8	12.4
		(117)	(113)	(130)	(144)	(115)	(149)
	TS (MPa)	24.0	24.1	19.6	19.8	21.5	21.8
		(96)	(99)	(90)	(93)	(91)	(90)
	EB (%)	505	495	490	485	480	490
		(93)	(93)	(78)	(77)	(87)	(83)
	TR ($N mm^{-1}$)	84	90	75	69	40	42
		(75)	(76)	(86)	(87)	(83)	(82)
3	M100 (MPa)	3.1	3.4	2.9	3.3	3.0	3.2
		(111)	(121)	(145)	(165)	(125)	(152)
	M300 (MPa)	11.8	11.9	10.7	11.6	11.8	12.5
		(109)	(110)	(151)	(161)	(125)	(151)
	TS (MPa)	21.1	20.0	19.6	18.9	21.0	21.7
		(84)	(82)	(90)	(88)	(89)	(90)
	EB (%)	470	400	470	425	460	430
		(86)	(75)	(75)	(67)	(84)	(73)
	TR ($N mm^{-1}$)	54	56	49	46	57	58
		(48)	(47)	(56)	(58)	(119)	(114)
4	M100 (MPa)	2.9	2.8	3.2	3.4	2.9	2.8
		(104)	(100)	(160)	(170)	(121)	(133)
	M300 (MPa)	11.4	11.1	11.5	12.1	11.4	11.1
		(106)	(103)	(162)	(168)	(121)	(133)
	TS (MPa)	20.3	19.8	18.1	17.3	20.3	19.8
		(81)	(81)	(83)	(81)	(86)	(82)
	EB (%)	460	455	455	395	460	455
		(84)	(85)	(72)	(63)	(84)	(77)
	TR ($N mm^{-1}$)	76	94	46	47	44	41
		(68)	(80)	(52)	(59)	(92)	(80)

[a] Figures within the parentheses indicate per cent retention of the properties.

for 14 days at 70 °C (Figs 10–12). As shown in Fig. 13, a slightly lower heat build-up value is observed for the Perkalink-containing compounds, compared to the reference when the base compound was cured up to 8t90, i.e. after anaerobic ageing. The reduction, and more so the stabilization of heat generation during dynamic flexing of unaged and aged samples, can be explained on the basis of a compensation of the loss of sulphidic cross-links leading to a stable modulus.

Heat build-up measured by Martin's ball fatigue tester is shown in Fig. 14. The importance of these results lies in the fact that the heat generated during the test is due to compression as well as shear of the sample. This test simulates actual service conditions of a tyre to a great degree. Under these conditions heat generation in the Perkalink 900-containing compound is lower than the corresponding control compound. It can be noted that the influence of Perkalink 900 is more pronounced in the case of cap 2 (based on a NR/BR blend) followed by cap 1 (based on 100% NR) and the base compound (100% NR with semi-efficient vulcanization system). These results strongly suggest that the addition of Perkalink 900 in the tread compounds will reduce heat generation during the service of a tyre.

3.4. Dynamic mechanical properties

Loss tangent values for the vulcanizates of cap 1, cap 2 and base compounds cured at t90, 2t90, 4t90 and

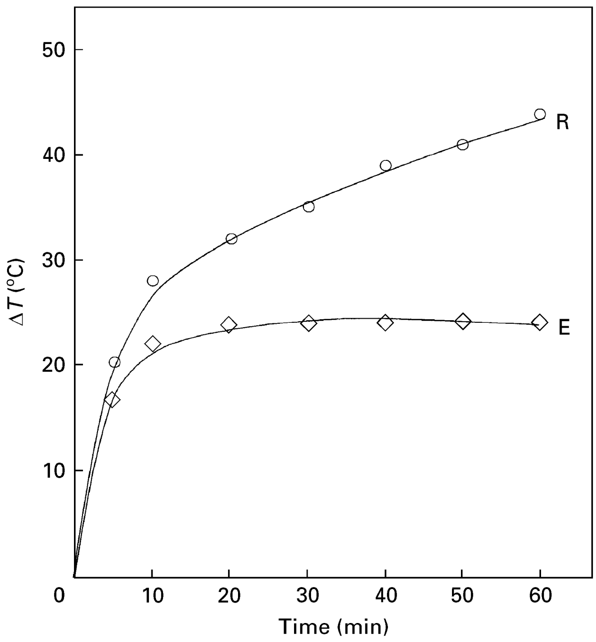


Figure 7 Heat build-up behaviour of the vulcanizate of cap 1.

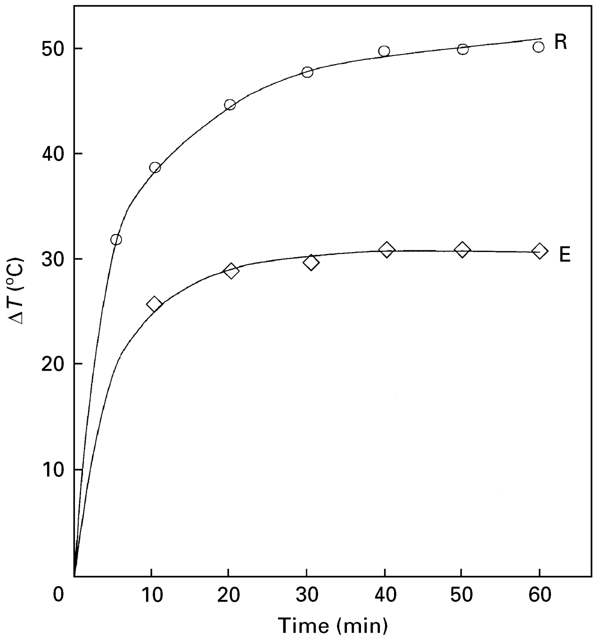


Figure 8 Heat build-up behaviour of the vulcanizate of cap 2.

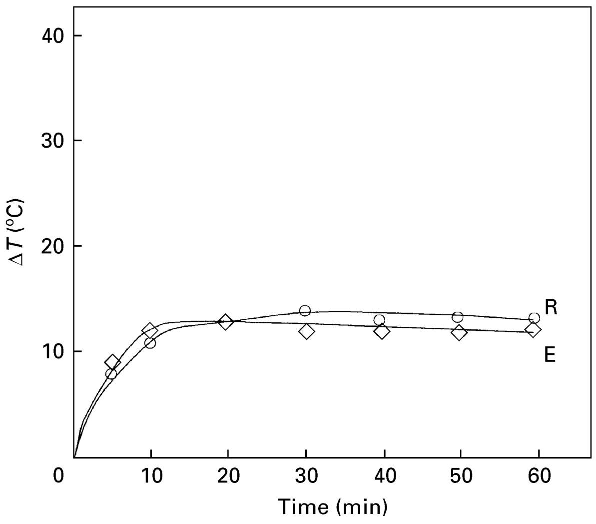


Figure 9 Heat build-up behaviour of the vulcanizate of base compound.

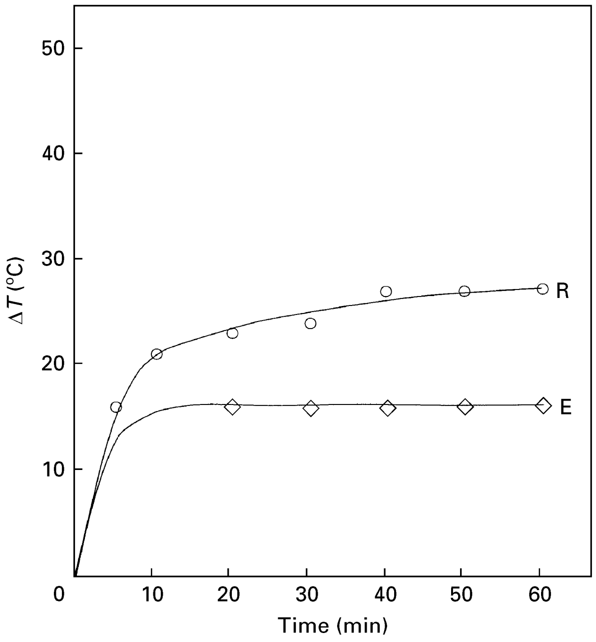


Figure 10 Heat build-up behaviour of the vulcanizate of cap 1 compound measured after ageing the sample at 70 °C for 2 wk.

8t90 were measured at 25 and 80 °C and at frequencies of 3.5 and 11 Hz, simulating the service conditions of tyre. The values are presented in Table V. It is evident from the data that the incorporation of Perkalink 900 invariably reduces the loss tangent. Because the rolling resistance of a compound is directly proportional to the loss tangent [17], it is expected that Perkalink 900 will favourably influence the rolling resistance of pneumatic tyres. It is interesting to note that the loss tangent values do not change considerably when the compounds are overcured, i.e. cured up to 2t90, 4t90 and 8t90 as shown in Table V.

3.5. Fatigue properties

Because this study was carried out on actual tyretread compounds, it is essential to observe the effect of Perkalink 900 on fatigue life and abrasion resistance. Fatigue to failure properties measured by a Monsanto fatigue to failure tester are illustrated in Fig. 15. It can be noted that the incorporation of Perkalink 900 in the compounds does not have an adverse effect on fatigue properties. This observation is also reflected with regard to modulus and elongation at break, the Perkalink 900 compounds maintaining closely the values for the control compounds under unaged conditions.

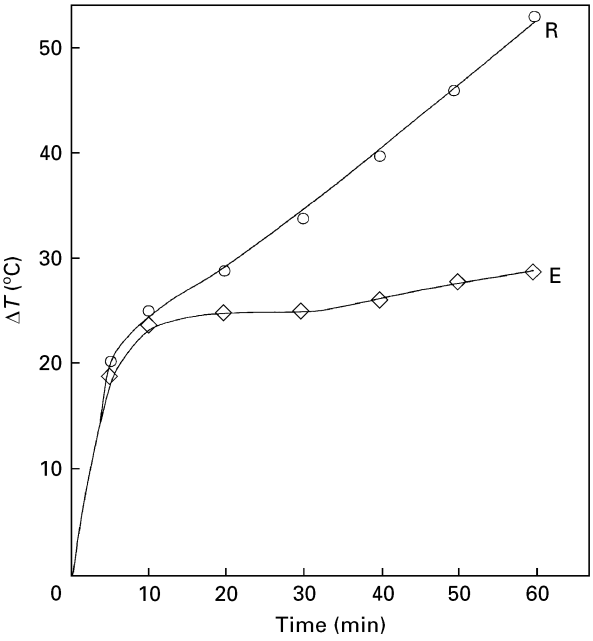


Figure 11 Heat build-up behaviour of the vulcanizate of cap 2 compound measured after ageing the sample at 70 °C for 2 wk.

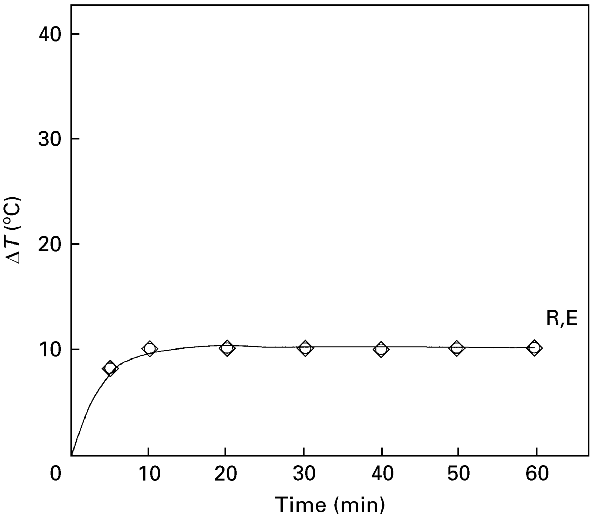


Figure 12 Heat build-up behaviour of the vulcanizate of base compound measured after ageing the sample at 70 °C for 2 wk.

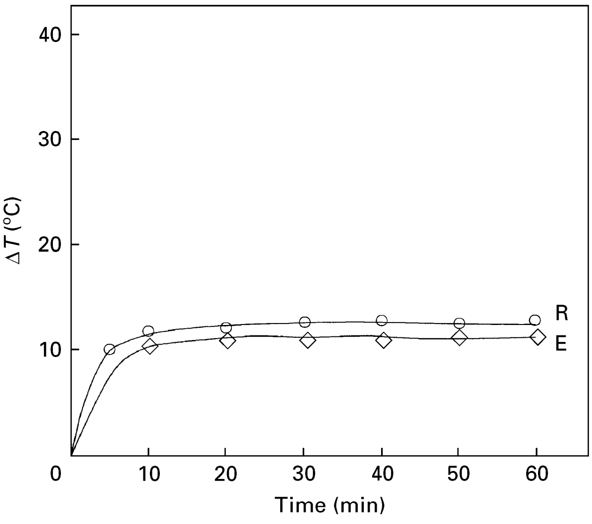


Figure 13 Heat build-up behaviour of the vulcanizate of base compound measured after curing the sample up to 8t90.

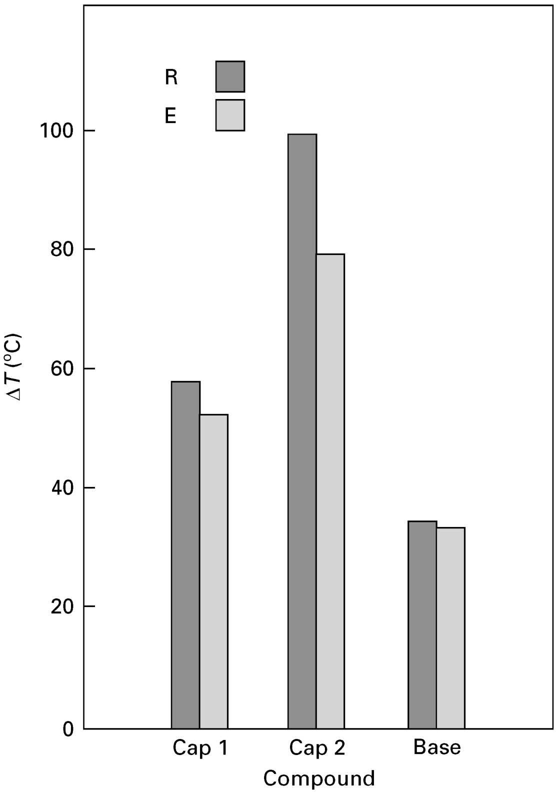


Figure 14 Heat build-up behaviour measured in Martin's ball fatigue tester.

3.6. Abrasion resistance

Abrasion resistance of the tread cap compounds is displayed in Fig. 16. It is clear that Perkalink 900 does not adversely affect abrasion resistance.

3.7. Mechanism and explanation of improved performance

The formation of conjugated dienes and trienes during reversion is well established [14, 18]. It has recently been reported [14] that Perkalink 900 reacts with these dienes and trienes via a double Diels Alder reaction, thus regenerating cross-links that are lost during reversion. The final effect is the compensation of destroyed cross-links and a reduction of diene/triene concentration in the network which will additionally improve vulcanizate properties. It has also been reported [19] that the cross-links formed by Perkalink 900 are relatively long; bond distance calculations show that Perkalink 900 cross-links are comparable to the length of S7 cross-links. Unlike short C–C cross-links, Perkalink 900 cross-links are expected to contribute towards improved dynamic properties. Our experimental findings lend support to the proposed mechanism of action of Perkalink 900.

4. Conclusions

The effect of Perkalink 900 has been studied in tread cap and base compounds of truck tyres. The

TABLE V Loss tangent values

Cure time (min)	Tan δ											
	Cap 1				Cap 2				Base			
	25 °C		80 °C		25 °C		80 °C		25 °C		80 °C	
	R	E	R	E	R	E	R	E	R	E	R	E
t90 3.5 Hz	0.34	0.30	0.29	0.25	0.31	0.30	0.25	0.24	0.14	0.12	0.11	0.09
11 Hz	0.33	0.29	0.28	0.24	0.31	0.29	0.24	0.24	0.13	0.11	0.10	0.09
2t90 3.5 Hz	0.33	0.30	0.28	0.26	0.32	0.32	0.25	0.25	0.13	0.10	0.10	0.09
11 Hz	0.33	0.30	0.27	0.25	0.31	0.31	0.25	0.24	0.12	0.08	0.10	0.09
4t90 3.5 Hz	0.33	0.30	0.30	0.26	0.25	0.25	0.33	0.31	0.13	0.11	0.10	0.10
11 Hz	0.33	0.29	0.30	0.25	0.32	0.27	0.30	0.24	0.12	0.10	0.08	0.09
8t90 3.5 Hz	0.33	0.32	0.28	0.26	0.33	0.29	0.30	0.25	0.13	0.11	0.11	0.09
11 Hz	0.33	0.33	0.28	0.25	0.33	0.28	0.30	0.24	0.12	0.10	0.10	0.08

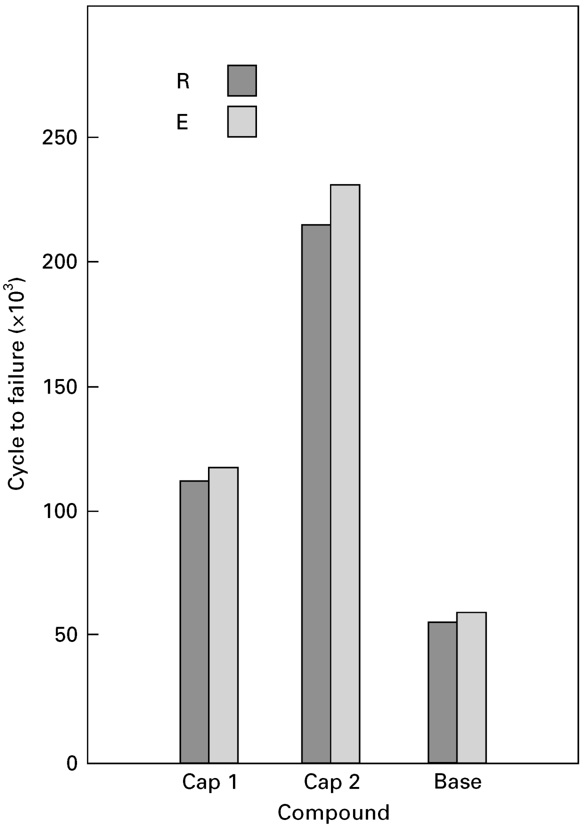


Figure 15 Fatigue to failure properties of cap 1, cap 2 and base compounds.

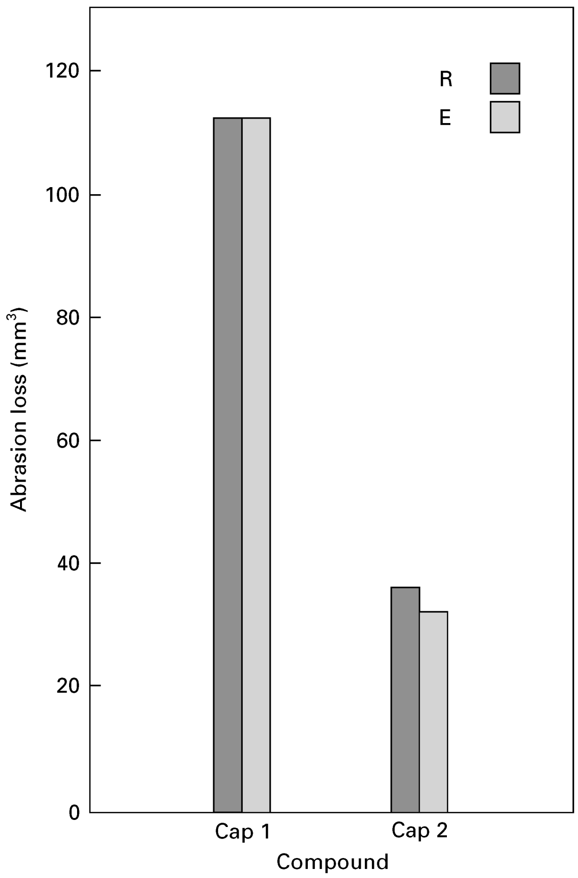


Figure 16 Abrasion resistance values of cap compounds.

incorporation of Perkalink 900 in these compounds gives a number of advantages compared to the control compounds.

1. A reduction or elimination of the reversion process when determined from cure characteristics is observed.

2. A higher retention of modulus and tensile strength after extended cure (anaerobic ageing) and hot air ageing (aerobic ageing) is noted.

3. A significant reduction in heat build-up, as measured in the Goodrich Flexometer, is observed for both the unaged and aged samples (aged 2 wk at 90 °C). This trend is maintained on extended cure of the base compound. A reduction in heat build-up is also observed in the Martin's ball fatigue test in which heat is generated due to compression and shearing of the sample.

4. An improvement in dynamic mechanical properties (tan δ), under conditions relevant to the service conditions of a tyre, is observed.

5. Fatigue to failure properties and abrasion resistance are maintained.

6. Perkalink 900 is shown to be a chemical that protects rubber compounds from the unwanted

reversion process. This unique compensation cure system enables the cross-link density under extended cure and hot-air ageing to be maintained.

Acknowledgements

The authors are grateful to the management of Hari Shankar Singhania Elastomer and Tyre Research Institute for allowing publication of this work. They are also grateful to Flexsys b.v., Netherlands for supplying Perkalink 900.

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Received 5 March 1996
and accepted 28 January 1997