

Networks · Stability · Ageing · Crosslink structure

When sulfur vulcanized natural rubber compounds are exposed to a thermal aging environment significant change in physical properties and performance characteristics are observed. These changes are directly related to modifications of the original crosslink structure. Decomposition reactions tend to predominate and thus leading to reduction in crosslink density and physical properties as observed during extended cure and when using higher curing temperatures. The decrease in network density is common when vulcanizates are subject to an anaerobic aging process. However, in the presence of oxygen, the network density is increased with the main chain modifications playing a vital role. The stability of the network during thermo-oxidative aging is a subject matter of this paper. Additionally, the effect of para-aramide on network is described with an emphasis on possible stabilization of network changes during oxidative aging.

Neue mechanistische Vorstellungen zur Netzwerkstabilisierung

Netzwerke · Stabilität · Alterung · Netzkonstruktion

Bei der Hitzealterung von NR Bauteilen werden signifikante Änderungen der physikalischen Eigenschaften beobachtet, die direkt aus den Änderungen der ursprünglichen Netzknotenstruktur ableitbar sind. Zersetzungsreaktionen überwiegen hierbei, wodurch eine Verminderung der Vernetzungsdichte und der physikalischen Eigenschaften bei längeren Vernetzungszeiten und höheren Temperaturen ausgelöst werden. Die Abnahme der Vernetzungsdichte tritt bei anaeroben Alterungsprozessen häufiger auf. Hingegen wird die Vernetzungsdichte in Gegenwart von Sauerstoff erhöht, wobei Hauptkettenmodifikationen von Bedeutung sind. Die Netzwerkstabilität bei thermisch-oxidativer Alterung ist der Gegenstand dieser Veröffentlichung. Der Effekt im para-Aramid auf das Netzwerk und die Möglichkeiten zur Stabilisierung von Netzwerkänderungen der oxidativen Alterung werden beschrieben.

New Mechanistic View on Network Stabilization

Truck and off-the-road tires of today are frequently required to operate at high loads and high speeds for extended periods of time. These severe operating conditions result in greater heat build up than would normally be encountered under less demanding service conditions. As a consequence, the excessive running temperature leads to reversion in compound components which may in turn lead to reduced tire durability or, in extreme circumstances, to tire failure.

Much effort has been spent over the years to improve the reversion characteristics of tire compounds. An established and, probably, best known approach is the use of so-called semi-efficient cure systems comprising reduced sulfur levels and increased accelerator levels. However, though effective in improving the vulcanizate's resistance to reversion, this approach is only partially successful since lowering of sulfur levels negatively influences other desirable properties such as tear and flex/fatigue life. With the advent of the radial tire, natural rubber (NR) usage has increased significantly. Its tack and high green strength serve to maintain green tire uniformity during building and shaping operations.

For both new and retreaded truck tires, however, the reversion characteristics of NR have been considered to detract from wear performance, particularly in the early stages of tire life where the tread surface has been subjected to the greatest degree of overcure. Accelerated wear in later tire life may also occur due to thermal-oxidative degradation of the vulcanizate, particularly cured with conventional systems. The need for chemicals that provide reversion resistance is, therefore, of great interest. Recently Datta [1] provided an extensive overview on approaches to improve reversion resistance through the use of antireversion chemicals, with emphasis on their applicability in truck tire tread compounds. These antireversion chemicals are:

- b) Dithiophosphate accelerators (Vocol ZBPD)
- c) Zinc soap activators (Struktol A73)
- d) Silane coupling agent, TESPT
- e) Post vulcanization stabilizer, Duralink® HTS
- f) Antireversion agent, Perkalink® 900
- g) 1,6-bis (N,N-dibenzylthiocarbamoyldithio) hexane, BDTCH, Vulcuren KA 9188

Fig. 1 illustrates the structural formula of these compounds.

In this paper the stability of network structure during oxidative aging process is addressed. A novel chemical, N-Cyclohexyl-4,6-Dimethyl-2-Pyrimidine Sulfenamide (CDMPS) is recently introduced to address the changes in the network experienced during service environments. The structure of CDMPS is shown in *fig. 2*.

Additionally, the effect of aramide short fiber on the network structure is explored. The aramid used in this investigation are:

- poly-(metaphenylene isophthalamide), MPIA (Teijin Conex)
- Co-poly-(para/3,4'-oxydiphenylene terephthalamide), Technora

The chemical structures of Teijin Conex and Technora are shown in *fig. 3*.

Experimental

Compound formulations are shown in the respective data tables. Compound mixing was carried out in a similar manner as described earlier [2].



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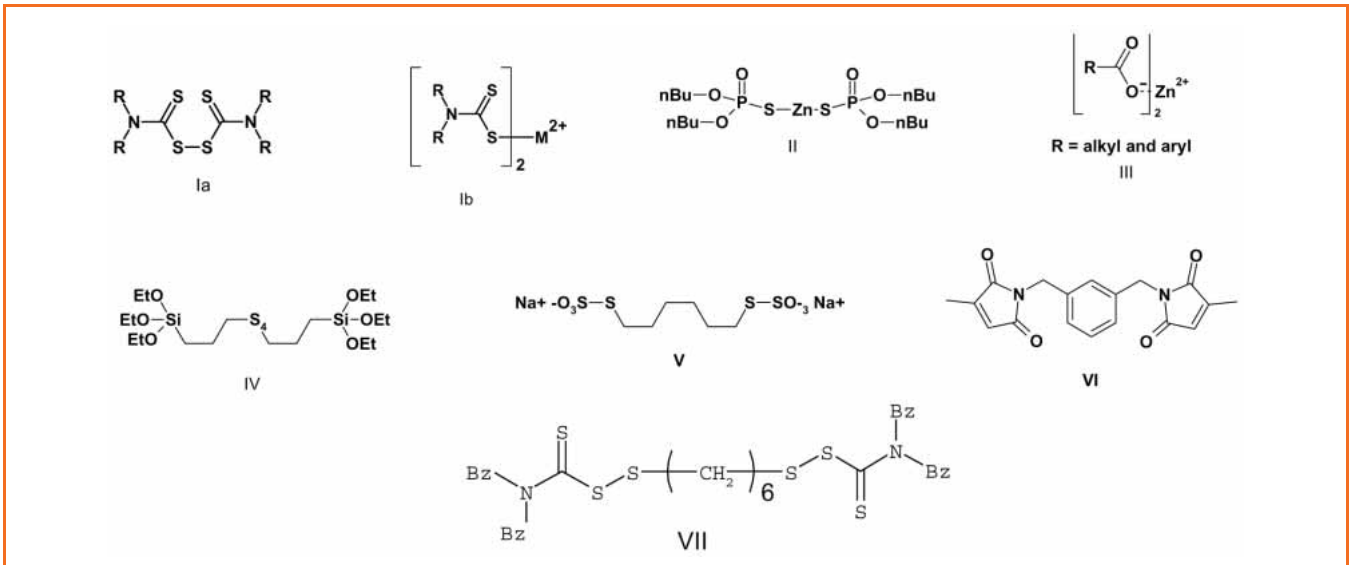


Fig. 1. Structures of Thiuram (Ia), Dithiocarbamate (Ib), Dithiophosphate (II), Zinc soap activator (III), Silane coupling agent (IV), Post vulcanization stabilizer, HTS (V), Antireversion agent, Perkalink 900 (VI), BDTCH, Vulcuren 9188 (VII)

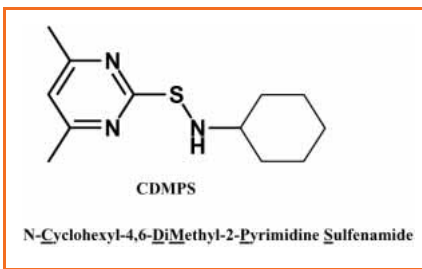


Fig. 2. Structure of Cyclohexyl-4,6-Dimethyl-2-Pyrimidine Sulfenamide (CDMPS)

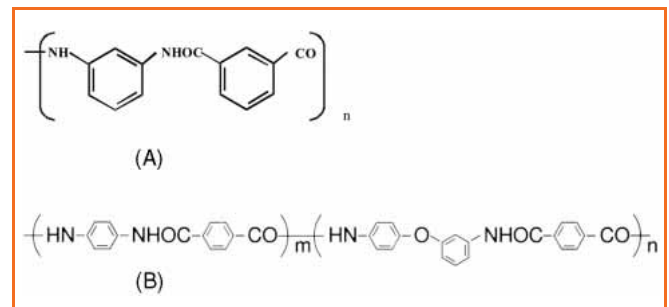


Fig. 3. Chemical structures of (A) Teijin Conex and (B) Technora

Stress strain and tear properties of the vulcanizates were measured using a Zwick universal testing machine (model 1445) in accordance with ISO 37 and ISO 34 respectively. Heat build up was measured on a Goodrich Flexometer according to the method described in ASTM D623. Fatigue

to failure properties were measured on a Monsanto Fatigue to Failure tester at 23 °C and 1.67 Hz with 0–100% extension.

The volume fraction (Vr) in the swollen vulcanizate was determined by equilibrium swelling in toluene using the method re-

ported by Ellis and Welding [3]. The Vr value so obtained was converted to the Mooney-Rivlin elastic constant (C_1) and finally to the concentration of chemical crosslinks by using equations described in the literature [4, 5]. The proportions of mono, di, polysulfidic and carbon-carbon crosslinks

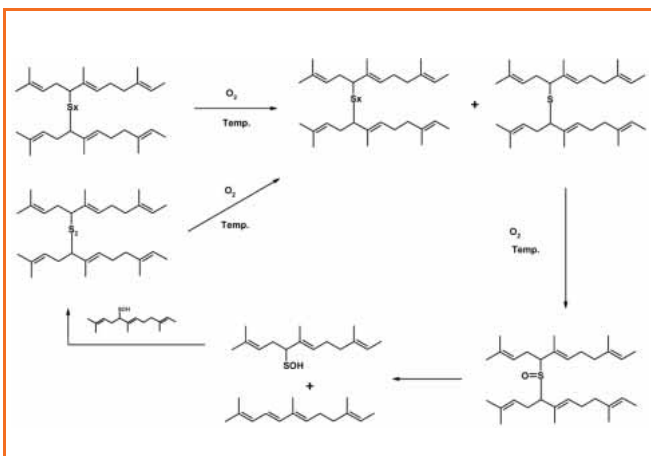


Fig. 4. Reaction of monosulfides with oxygen/heat forming additional crosslinks

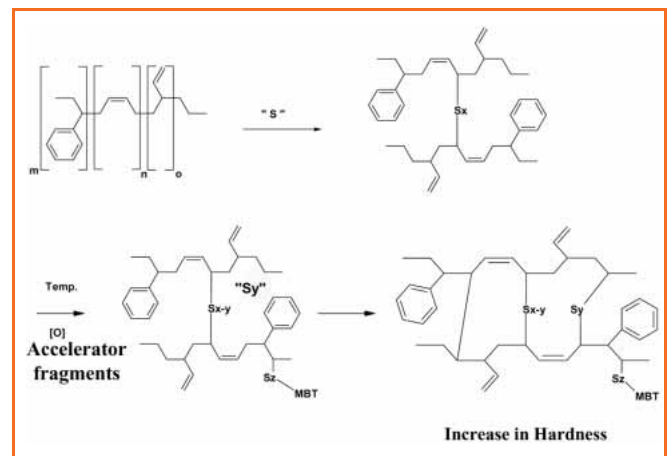


Fig. 5. Reaction of Polysulfides with oxygen/heat forming additional crosslinks

were determined using the method reported elsewhere [2].

HPLC was used to determine the accelerator residue in model vulcanization. Details of HPLC conditions are summarized below:

Guard column:

Reversed phase packing

Analytical column:

Lichrospher 100 RP-18, 125*4 mm, 5 µm

Mobile phase:

A: 75 volume % of 0.01 M ammonium acetate in water and 25 volume % methanol with 0.1% acetic acid. Filtered and degassed

Gradient:

0 min: 95% A

60 min: 0% A

70 min: 0% A

71 min: 95% A

75 min: 95% A

Flow rate: 1 ml/min

Oven: 25 °C

Injection volume: 10 µl

Detection: UV at 280 nm

Results and discussion

Protection against degradation in oxidative aging environments: Effect of *N*-Cyclohexyl-4,6-Dimethyl-2-Pyrimidine Sulfenamide (CDMPS)

One of the burning demands in the rubber industry has been to reduce the changes in the network during the service life of rubber components. In a broad sense, this is also considered as degradation (reversion) of network but under oxidative environments. The changes in the network under aerobic conditions are different in nature than experienced under anaerobic conditions. In a true sense, the rubber compounds experience hardening effects in the presence of oxygen and heat.

The process of hardening or increase in modulus or increase in crosslink density is as a result of oxidation of sulfidic crosslinks, liberation of active sulfur and consequently re-crosslinking. The process is schematically shown in *fig. 4*.

It is well known that the degradation of polysulfides is catalyzed by the presence of accelerators (*fig. 4*). The liberated active sulfur is responsible for introduction of additional crosslinks and hence increases in modulus.

In order to reduce the unwanted hardening effects during oxidative aging, the

trap or removal of accelerator fragments is desirable. Over the years, focus was on the development of an accelerator, which becomes inactive after the vulcanization and thereby decreases the kinetics

of degradation of polysulfides. The research culminated in a development of a novel accelerator, *N*-Cyclohexyl-4,6-Dimethyl-2-pyrimidine Sulfenamide [6].

Tab. 1. Summary of advantage of CDMPS over conventional accelerator

SBR-BR Passenger Tread					
(Summary)					
Rheo; 160 °C	Control	CDMPS			
Delta S, Nm	1.14	1.15		Control	CDMPS
Ts2, min	10	12	CBS	1.3	0
t90, min	4.3	4.5	CDMPS	0	1.3
			MBT	0	0.5
Cure: 160 °C/t90			Sulfur	2	2
(Changes after aging*)	3d/100 °C				
Hardness, IRHD	+ 11	+ 6			
MS* (based on M200%), %	+ 220	+ 158			
Elongation drop, %	- 39	- 22			
Flex, % (Constant stress)	- 35	- 10			
Tangent delta, - 20 °C, %	- 20	- 3			

Masterbatch: SBR 1712, 137.5; N-220, 60; Zinc oxide, 3.0; Stearic acid, 2.0; 6PPD, 1.0

* MS, % = (Aged M200/Unaged M200) × 100

Tab. 2. Crosslink density (Cure: 160 °C/t90)

XL-densities* × 10 ⁵	Control	CDMPS
<i>Unaged</i>		
Total	3.79	3.82
Poly-S	1.95	2.08
Di-S	0.53	0.56
Mono-S	1.31	1.18
ZnS × 10 ²	0.550	0.540
<i>Aged, 3d/100 °C</i>		
Total	5.15	4.30
Poly-S	0.64	1.05
Di-S	0.15	0.30
Mono-S	4.36	2.95
ZnS* × 10 ²	0.587	0.727

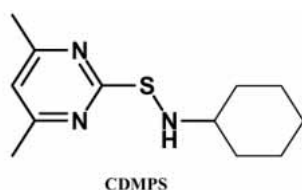
* Crosslink density expressed in gram mole/gram rubber hydrocarbon

* Zinc sulfide sulfur expressed in gram/gram rubber hydrocarbon

Tab. 3. Formulation (model truck tread)

Ingredients	1	2	3	4	5
NR SMR CV	80	80	80	80	80
BR Buna CB 10	20	20	20	20	20
TOR Vestenamer 8012	2.5	2.5	2.5	2.5	2.5
Carbon black, N-375	40	36	36	36	36
Carbon black, N-660	5	5	5	5	5
Aromatic Oil	8	8	8	8	8
Zinc oxide	4	4	4	4	4
Stearic acid	2	2	2	2	2
Santoflex 6PPD	2	2	2	2	2
Conex CF 1 mm	0	0	0	0	0
Conex DCF 1 mm	0	0	1	0	0
Technora CF 1 mm	0	0	0	1	0
Technora DCF 1 mm	0	0	0	0	0
Santocure TBBS	0.7	0.7	0.7	0.7	0.7
Sulfur	2.3	2.3	2.3	2.3	2.3

CF and DCF refer to chopped and dip-chopped fiber respectively



N-Cyclohexyl-4,6-DiMethyl-2-Pyrimidine Sulfenamide

CDMPS has been tested in several compounds where the effect on modulus increase during oxidative ageing is monitored. Some typical data are shown in *Table 1*.

It is clear from the data that the changes in hardness and modulus during oxidative ageing are considerably reduced. The resistance to hardness increase positively influences the dynamic properties as shown in *Table 1*.

In order to understand the changes in the network during oxidative ageing in the presence of CDMPS, some network studies were carried out. Data are tabulated in *Table 2*.

The increase in crosslink density upon oxidative ageing is minimized in the presence of CDMPS. The level of zinc sulfide is higher indicating that part of sulfur kicked out during the ageing process is trapped by zinc as zinc sulfide. The mechanism of the process is proposed as shown in *fig. 6*. That the accelerator residues are minimized when CDMPS was used as an accelerator in lieu of conventional sulfenamides, such as N-cyclohexyl-2-benzothiazole sulfenamide (CBS) or N-ter. butyl -2-benzothiazole sulfenamide (TBBS) is well demonstrated by comparing the HPLC chromatograms as shown in *fig. 8* and *9*. In order to elucidate the mechanism, model olefin, such as 5-phenylhex-2-ene (*fig. 7*) was used as a representative for E-SBR.

It is clear from *fig. 8* that relatively large amount of 2-mercatobenzothiazole (MBT) accelerator residues are present within the rubber matrix and this is capable of desulfurating the polysulfidic crosslinks generating new crosslinks and hence hardening takes place. The component P1 and P2 are identified as monosulfidic crosslinks and pendate accelerator moieties respectively.

In the case of vulcanization by CDMPS, the thiol 4,6 dimethyl-2-mercaptopyrimide (DMMP) is present in relatively lower proportion as compared to vulcanization carried out by CBS/S cure system. Additionally, 4,6 dimethyl-2-pyrimidine disulfide (DMMPs) is formed but in relatively low proportions. *Fig. 9* demonstrate the fact.

Tab. 4. Distribution of crosslink types (Cure: 160 °C/t90)

Crosslinks*	1 Control	2 Conex CF	3 Conex DCF	4 Tech. CF	5 Tech. DCF
Total	5.20	5.22	5.30	5.33	5.40
Polysulfidic	4.15	3.81	3.22	3.77	3.10
Disulfidic	0.88	0.92	1.01	0.95	1.10
Monosulfidic	0.17	0.49	1.07	0.61	1.20

* expressed in g mole/ g rubber $\times 10^5$

Tab. 5. Heat build up at 100 °C (Load 11 kg, Stroke: 4.45 mm and duration 2 h)

	1 Control	2 Conex CF	3 Conex DCF	4 Tech. CF	5 Tech. DCF
Temp. increase, °C	80	66	64	62	57
Permanent set, %	30	22	21	20	17

Tab. 6. Viscoelastic properties (temp. 60 °C; strain: 1% and Frequency: 15 Hz)

	1 Control	2 Conex CF	3 Conex DCF	4 Tech. CF	5 Tech. DCF
E', MPa	7.52	7.70	7.38	7.44	7.01
E'', MPa	1.03	1.01	0.91	0.88	0.74
Tangent delta	0.137	0.132	0.123	0.119	0.105

Tab. 7. Changes in crosslink structure upon oxidative ageing

Crosslinks*	1 Control	2 Conex CF	3 Conex DCF	4 Tech. CF	5 Tech. DCF
Unaged					
Total	5.20	5.22	5.30	5.33	5.40
Polysulfidic	4.15	3.81	3.22	3.77	3.10
Disulfidic	0.88	0.92	1.01	0.95	1.10
Monosulfidic	0.17	0.49	1.07	0.61	1.20
Aged 3d/100 °C					
Total	6.30	5.90	5.50	5.78	5.62
Polysulfidic	1.15	1.55	2.01	1.65	2.20
Disulfidic	0.33	0.55	0.65	0.66	0.75
Monosulfidic	4.82	3.82	2.84	3.47	2.67

* expressed in g mole/ g rubber hydrocarbon $\times 10^5$

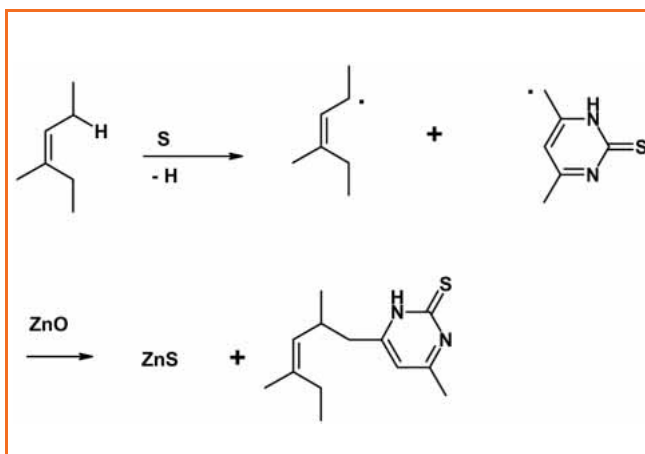


Fig. 6. Formation of zinc sulfide and trapping of accelerator's rest

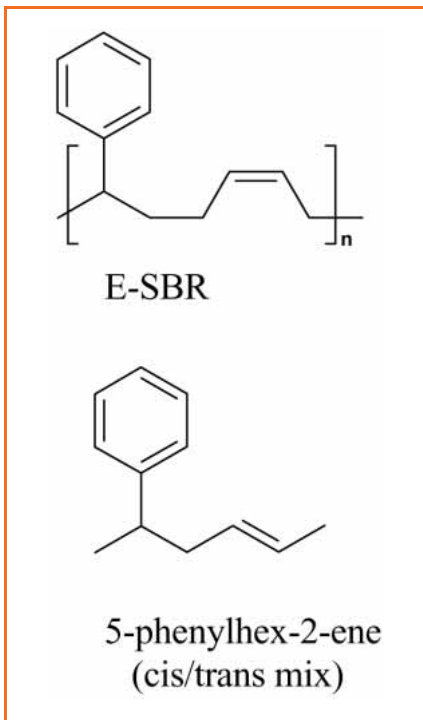


Fig. 7. Structures of model, 5-phenylhex-2-ene and E-SBR

Comparing the two HPLC chromatograms (fig. 8 and 9), it is also clear that in the presence of CDMPS, the pendant accelerator group (analogous to P2 for CBS) is absent signifying less desulfuration of polysulfidic crosslinks.

It can be inferred therefore that the mechanism of CBS and CDMPS is different in vulcanization process. CDMPS is trapped, whereas large amount of accelerator residue still present when vulcanization is carried out with CBS accelerator.

Protection against degradation in oxidative aging environments: Effect of Aramid short fibers

Changes in network by using short Fibers from Aramid (Conex and Technora) are studied in typical truck tread compounds. Table 3 shows the formulation. When using Aramid in the mix, the level of black was slightly decreased in order to maintain the modulus of the resulting compounds. The data concerning network structure are shown in Table 4.

It is clear that both Conex and Technora change the network towards maturation, which results in better thermal stability resulting in lower heat build up and improved dynamic properties (Tables 5 and 6).

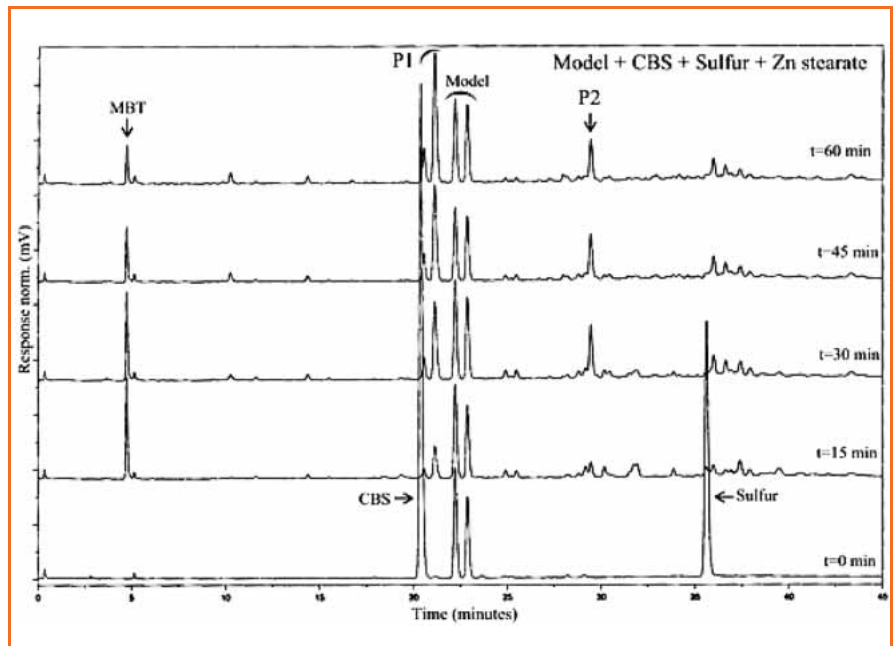


Fig. 8. Reaction of model, zinc stearate, CBS and Sulfur heated to 160°C monitored by HPLC

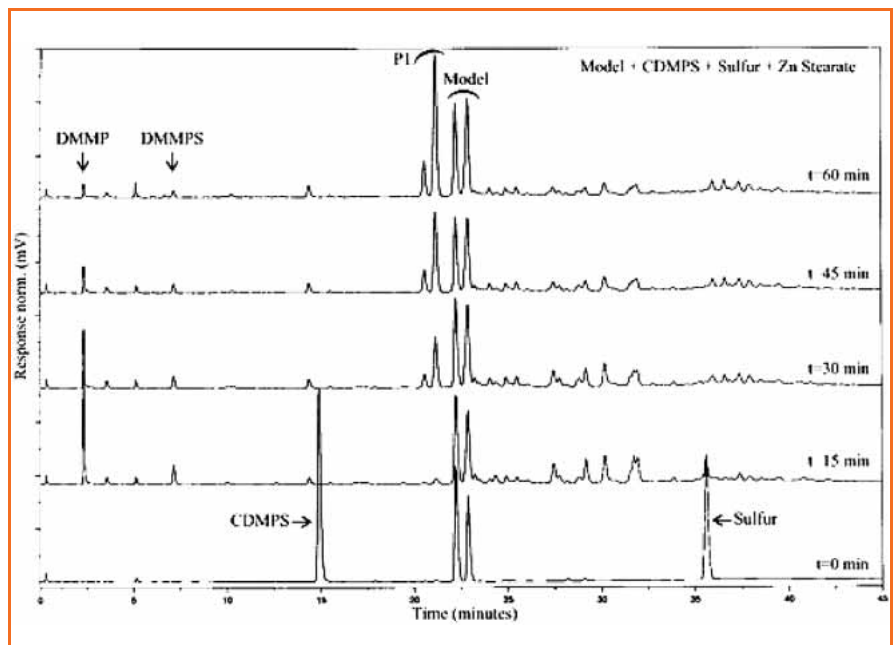


Fig. 9. Reaction of model, zinc stearate, CDMPS and Sulfur heated to 160°C monitored by HPLC

This is in line with earlier studies carried out by Rijpkema [7].

The formation of mature network might be due to an additional zinc complex formation shown in fig. 10, which could participate in the desulfuration reaction of initially formed poly-sulfide network.

The network changes during aerobic ageing are tabulated in Table 7.

The data shown in Table 7 clearly indicate that the aramid short fibers stabilize the

network changes following oxidative ageing environment.

Summary

Two new approaches are described to stabilize the network changes following thermo-oxidative service environments.

The new accelerator, CDMPS restricts the modulus and hardness increase during the oxidative ageing process. Data sug-

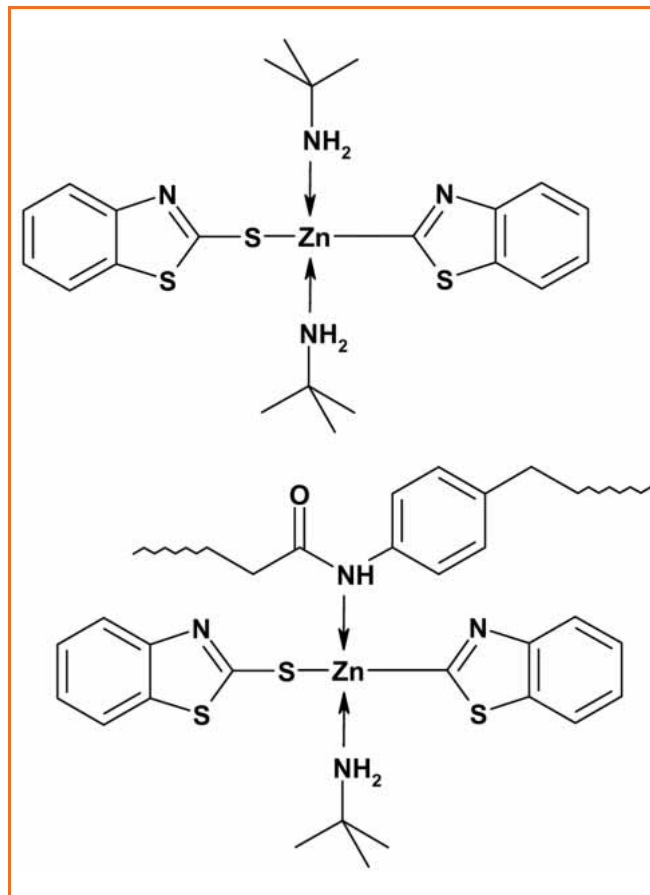


Fig. 10. Probable zinc complexes from accelerator and amine-terminated amide

gests that the accelerator is capable of maintaining the initially formed crosslinks thereby keeping changes in compound properties at a minimum.

The use of aramid short fibers stabilizes changes in network probably by maturation of initially formed network. The resulting network provides better chipping-chunking resistance, Flex-fatigue and other dynamic properties.

Combining the possibilities as outlined above, it is now possible to optimise a compound with improved heat stability under aerobic environments.

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