Study of Metal Poisoning in Natural Rubber–Based Tire-Tread Compound

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ABSTRACT: In the present study the effect of metal poisoning was studied in a natural rubber (NR)–based tire-tread compound. The experimental compound contained 1000 ppm copper metal as an additional ingredient. A detailed study was carried out and the results of the experimental compound were compared against a control compound having no metal ion. The effect of metal poisoning was not significant in the case of the green experimental compound, even after prolonged storage of 150 days. However, the cured experimental compound deteriorated substantially after ageing in aerobic-, anaerobic-, oil-, and out-door-ageing conditions. The ozone resistance property of the experimental compound also proved to be inferior. The degradation kinetic of metal poisoning was found to be a first-order reaction and the service life (as expressed by the half-life period) was drastically reduced for the poisoned compound. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 1492–1499, 2005

Key words: metal poison; crosslinking; volume fraction; ageing; rheology

INTRODUCTION

Different metals, particularly transition metals, are characterized as poison with respect to rubber. The different sources of metals, which have variable oxidation states, are impurities present in different raw materials used in the tire industry and also the catalysts used in the polymerization process for manufacturing of different polymers. Natural rubber also contains metallic impurities arising out of nature itself. These metals are hydroperoxide decomposers. The catalytic mechanism of hydroperoxide decomposition was previously reported.[1,2]

Uncoated TiO_2 is reported to cause melt degradation of polyethylene.[3] Polyolefins readily degraded as a result of formation of metal carboxylate.[4] The effect of copper on a gum compound of oil-extended styrene butadiene rubber (SBR) and the effect of cobalt on the stability of divinyl rubber was also previously reported.[5] Different commercially available metal deactivators are being used nowadays in polymeric goods to reduce the activity of metal poisons. It is believed that metal poisoning is more destructive in polymers containing unsaturated backbone.[6]

Within the tire industry worldwide, a strict specification is maintained to restrict transition metals, specifically copper, iron, manganese, chromium, lead, and cadmium, present in different raw materials.

The study reported in the present article details the effect of metal poisoning on a natural rubber–based tire-tread compound. A comparative study was made between a control compound without metal and an experimental, highly poisonous compound having 1000 ppm copper. The study with respect to rheometric, unaged physical, and retention of physical properties after ageing under different environmental conditions, abrasion loss, swell index, volume fraction, dynamic mechanical property, and ozone resistance was done. The kinetics of deterioration of rubber compound was also studied. The service life (as expressed by a half-life period) was also determined for both compounds.

EXPERIMENTAL

Suppliers of all materials used in this study are listed in Table I and compound formulations are given in Table II.

Other ingredients used in the compound formulations, kept at constant loadings, were [parts per hundred rubber (phr)]: PCTP, 0.20; N330 Black, 45; ZnO, 4.0; stearic acid, 2.0; 6PPD, 2.0; TMQ, 1.0; aromatic oil, 6.0; soluble sulfur, 2.0; NOBS, 0.75; PVI 100, 0.20.

TABLE I
Materials Used and Their Sources

Sample	Material	Supplier
1	Natural rubber, sheet rubber, RSS 3	MARDEC International, Malaysia
2	PCTP (pentachlorothiophenol)–based peptizer, PEPTIZOL-7	Acmechem Limited, Ankeleshwar, India
3	High-abrasion furnace black (HAF, N330)	Cabot India Ltd., Mumbai, India
4	Aromatic oil, RPO 701	Sah Petroleum Limited, Daman, India
5	Red seal zinc oxide	Zinc-O-India, Ltd., Alwar, Rajasthan, India
6	Stearic acid	Godrej Industries Ltd., Mumbai, India
7	Antiozonant, 1,3-dimethylbutylpara-phenylene diamine, 6PPD, PILFLEX 13	NOCIL, Thane, India
8	Antioxidant, 1,2-dihydro-2,4,6-tri-methyl quinoline, TMQ, PILNOX TDQ	NOCIL, Thane, India
9	Rubber makers sulfur (soluble sulfur)	Jain Chemicals, Kanpur, India
10	Accelerator, N-oxydiethylenebenzo-thiazyl/sulfenamide,/NOBS, PILCURE MOR	NOCIL, Thane, India
11	Scorch inhibitor, N-cyclohexylthio-pthalimide, CTP (prevulcanizing inhibitor, PVI 100), ACCITARD RE	ICI, Rishra, India
12	Copper sulfate salt	Mark, India

Mixing of rubber compounds

The mixing of the rubber compounds was done using a two-wing rotor laboratory Banbury mixer of 1.5 L capacity (Kobelco Stewart Bolling, Hudson, OH), in two stages (masterbatch and final batch). In the masterbatch mixing, the temperature control unit (TCU) of the Banbury mixer was kept at 90°C and the rotor speed maintained at 60 rpm. The rubber, along with a peptizer, was added and the mixture was premasticated for around 45 s. This was followed by addition of carbon black, oil, zinc oxide, stearic acid, and anti-degradants including copper sulfate for the experimental compound. The ram was scraped between additions and, after an attainment of 0.36 kWh power at the power integrator (PI), the batch was dumped. The dump temperature of the masterbatches was found to be within 145–155°C. After a maturation time of 4 h the final batch compound was mixed. In the final stage, the TCU of the Banbury mixer was kept at 60°C and the rotor speed at 30 rpm. The curing agents (sulfur, accelerator, and scorch inhibitor) were added to the masterbatch compound and batches were dumped after an attainment of 0.12 kWh power at the power integrator. The dump temperature of the final batches was within 95–105°C. After each mixing stage, the batches were sheeted out in a laboratory two-roll mill (Santosh Industries, New Delhi, India).

Rheometric property study

The rheometric characteristics were carried out in a moving-die rheometer (MDR 2000E, Alpha Technolo-gies, Akron, OH) in accordance with ASTM D5289 at 141°C for 1 h, maintaining a 0.5° arc.

Storage stability

The storage stability of the green rubber compounds was also determined from the maximum torque value after exposing the green compounds to laboratory conditions for 150 days.

Sample preparation

The green rubber compounds were cured in accordance with ASTM D3182 in an electrically heated hydraulic curing press (Hind Hydraulics, New Delhi, India) using compression molding. The molding condition followed for stress–strain properties was 141°C for 45 min, during which a 14.5 MPa gauge pressure was maintained. The tensile samples were subject to Die C processing according to ASTM D412.

TABLE II
Compound Formulation

Ingredient	Compound	
	Control	Experimental
NR, RSS # 3, phr	100	100
Copper ion, ppm (with respect to rubber) as $CuSO_4 \cdot 5H_2O$	—	1000

TABLE III
Rheometric Properties

Test parameter	Compound	
	Control	Experimental
Minimum torque (dN-m)	2.64	2.94
Maximum torque (dN-m)	15.83	15.93
ts_2, scorch safety time (min)	11.21	8.27
Tc_{90}, optimum cure time (min)	26.86	25.13

Ageing conditions

The tensile samples were aerobic aged at 70°C for 2, 4, and 6 weeks and at 105°C for 24 h in a multicell ageing oven from Tempo Industries (New Delhi, India) and in anaerobic-ageing condition at 130°C for 16 h in a closed mold. The oil ageing of the tensile samples was carried out in accordance with ASTM D471 in ASTM Oil 2. Outdoor ageing was carried out for a period of 90 days in accordance with ASTM D1171. The samples for dynamic mechanical property testing were aged under aerobic condition at 70°C for 1 week. The samples for swell index and volume fraction testing were anaerobic aged at 105°C for 24 h. The samples for abrasion-loss testing were also aerobic aged at 70°C for 2 weeks.

Physical properties

The unaged and aged tensile properties were measured using a UTM 1445 apparatus (Zwick GmbH KG, Ulm, Germany) according to ASTM D412. The hardness was measured with a dead-load hardness tester (Wallace Instruments, Surrey, UK) according to ASTM D1415. The durometer hardness test was also carried out (ASTM D2240) using a Shore A durometer (Prolific Equipment, New Delhi, India). The unaged and aged abrasion-loss property at 10 N load was measured in a Zwick Din Abrader (ASTM D5963). In dynamic mechanical property testing, the original and aged tan δ values were measured at 100°C, 11 Hz frequency, and 5% strain level using a dynamic mechanical analyzer (Metravib RDS VA4000, MVI Technologies Group, Limonest, France) according to ASTM D5992. The ozone testing of the samples was carried out in accordance with ASTM D1149B under bent-loop mode and maintaining a 50 ± 5 ppm ozone concentration, 40°C temperature, and 20% strain level. The microphotographs of the ozone tested samples were taken using a Wild M10 optical microscope with image-analyzer software (Leica AG, Heerbrugg, Switzerland).

The swelling index of the cured samples was measured using the following formula in accordance with ASTM D3616:

$$\text{Swelling index} = \frac{\text{Swollen weight}}{\text{Initial weight}}$$

The volume fraction V_r of the insoluble rubber fraction in the swollen gel was calculated using the following formula[7–9]:

$$V_r = \frac{(d - fh)/\rho_r}{(d - fh)/\rho_r + (s - h)/\rho_s}$$

where V_r is the volume fraction; d is the weight of the deswollen sample; h is the initial dry weight of the sample; f is the weight fraction of insolubles in solvent; s is the swollen weight of the sample; and ρ_r and ρ_s represent density of the rubber and solvent, respectively.

Differential scanning calorimetric (DSC) study

The onset, peak temperature, and enthalpy of curing were measured using a 7 Series thermal analyzer system with DSC-7 model differential scanning calorimeter and Pyris software (Perkin–Elmer Cetus Instruments, Norwalk, CT).

(a)

(b)
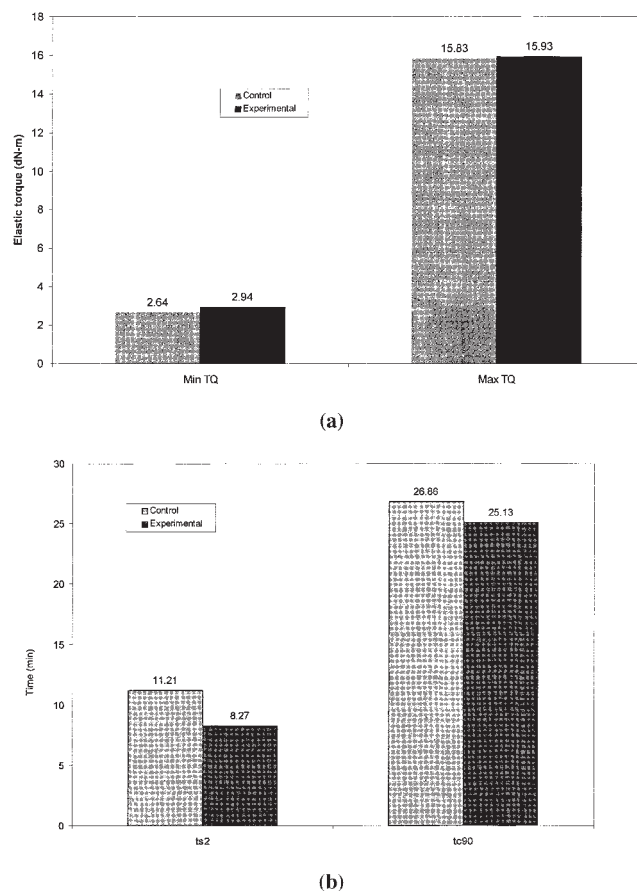
Figure 1 Effect of metal poisoning on rheometric properties (a) and (b).

TABLE IV
DSC Study

Test parameter	Compound	
	Control	Experimental
Enthalpy of curing (J/g)	9.6	5.0
Onset of curing (°C)	168.0	157.0
Peak temperature of curing (°C)	200.0	200.0

RESULTS AND DISCUSSION

The rheometric properties are given in Table III and also shown in Figure 1(a,b).

The scorch safety time for the experimental compound was lower than that of control. This is explained by the presence of copper, which acted as a cure activator in the presence of zinc oxide. It has been reported that copper reduces the scorch safety.[10] Copper is placed in the first transition metal series in the periodic table. It has a favorable crystal field stabilization energy (CFSE) in both tetrahedral and octahedral configuration compared to that of zinc.[11] As a result, copper will easily form the initial metal–accelerator chelate complex. Therefore, the early crosslinking will reduce the scorch safety and also reduce the activation energy for curing. The same observation was reported[12] when cobalt and a nickel-containing adhesion promoter were used. The lowering of activation energy and involvement of the metal ion in the rate-determining step of vulcanization was also reported.[12] No changes in other rheometric properties were observed.
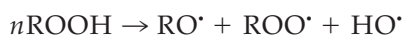
Results of the DSC study are given in Table IV.

The onset temperature of curing was shifted to lower values for the experimental compound and the enthalpy of curing also showed a similar trend for the experimental compound. The shifting of onset of curing temperature to lower values, as reported earlier,[12] also supports the involvement of copper ion in the early stage of reaction.

The tensile properties under different ageing conditions are shown in Figure 2(a–c).
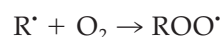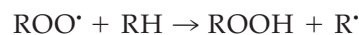
The experimental compound deteriorated rapidly compared to the control compound, which is attributed to the increase in rate of hydroperoxide decomposition (as described in the mechanism scheme in the following section) in the presence of copper. The degradation (oxidative and thermal) of a natural rubber is a complex process involving many reactions. The double bond is the primary point for initiating the degradation.

The simplified mechanism[13] for the degradation (oxidative, thermal) of natural rubber is as follows:
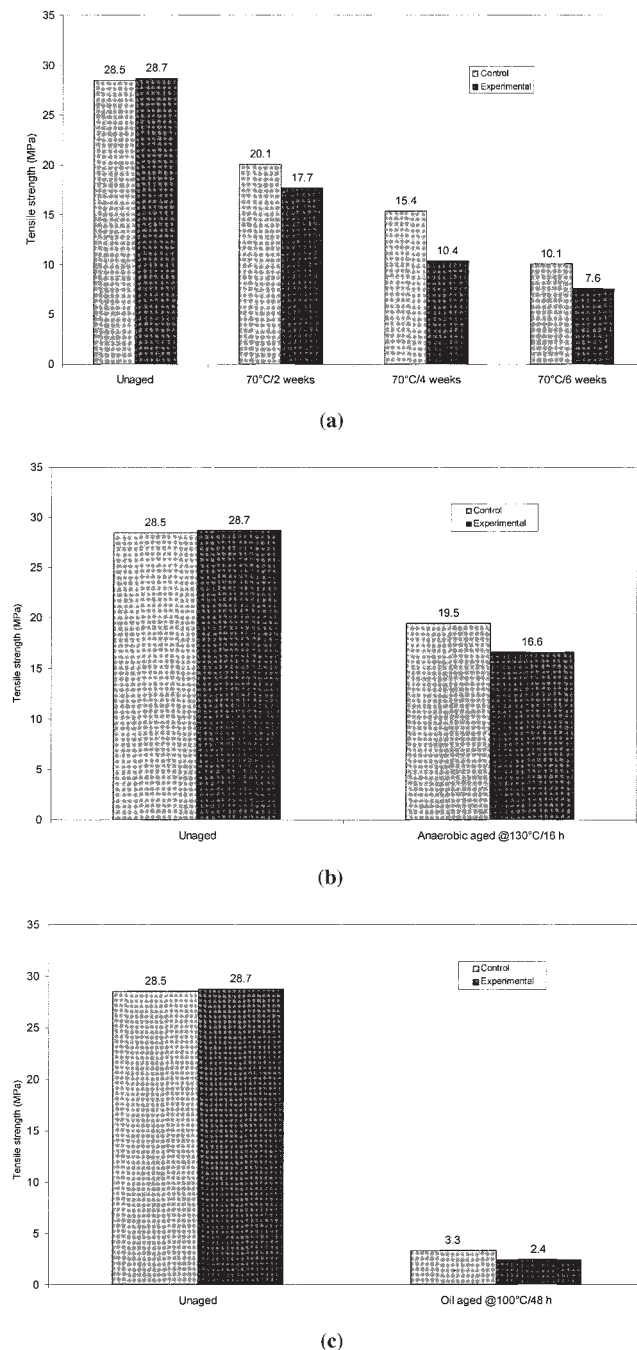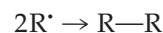
Initiation

$$R\!-\!R \rightarrow 2R^{\bullet}$$

$$n\text{ROOH} \rightarrow \text{RO}^{\bullet} + \text{ROO}^{\bullet} + \text{HO}^{\bullet}$$

Propagation

$$\text{ROO}^{\bullet} + \text{RH} \rightarrow \text{ROOH} + \text{R}^{\bullet}$$

$$\text{R}^{\bullet} + \text{O}_2 \rightarrow \text{ROO}^{\bullet}$$

Termination

$$2\text{R}^{\bullet} \rightarrow \text{R}\!-\!\text{R}$$

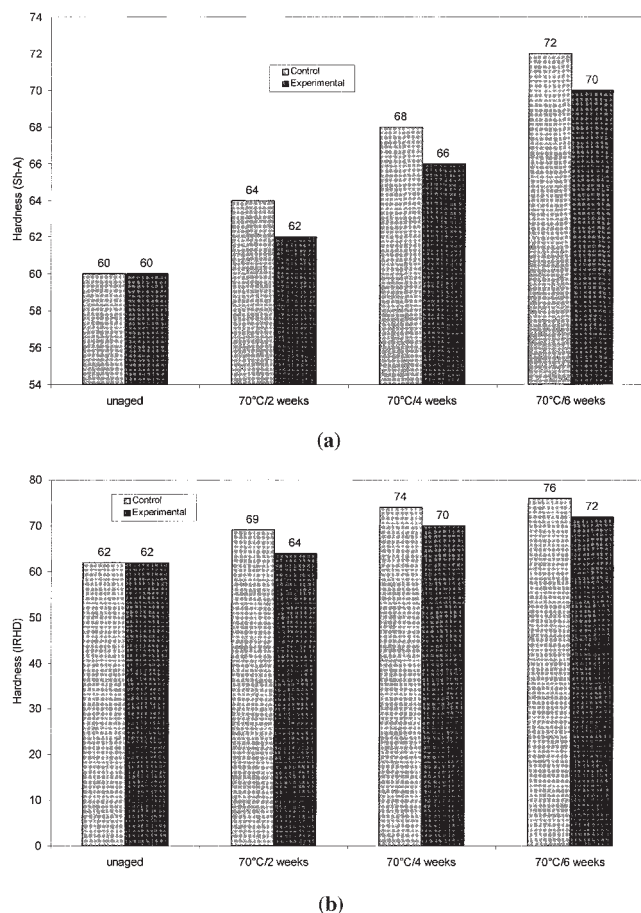$$\text{R}^{\bullet} + \text{ROO}^{\bullet} \rightarrow \text{ROOR}$$

(a)

(b)

(c)

Figure 2 Effect of metal poisoning on (a) aerobic-aged tensile strength, (b) anaerobic-aged tensile strength; (c) oil-aged tensile strength.
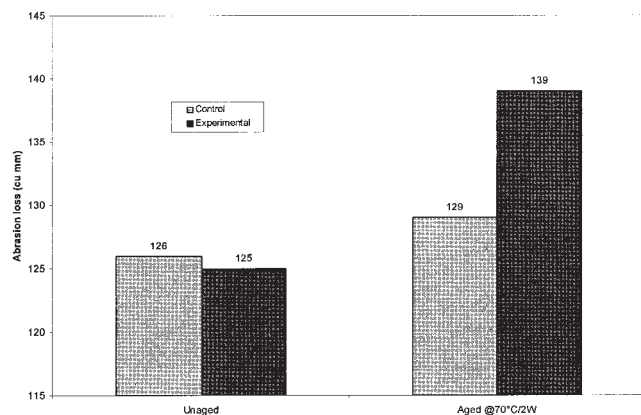
(a)

(b)

Figure 3 Effect of metal poisoning on air-aged hardness: (a) Sh-A and (b) IRHD.

$$2ROO^{\bullet} \rightarrow \text{Nonradical product} + O_2$$

The first reaction is important only in the very early stage of oxidation. The hydroperoxide is the kinetically important initiator.[14]

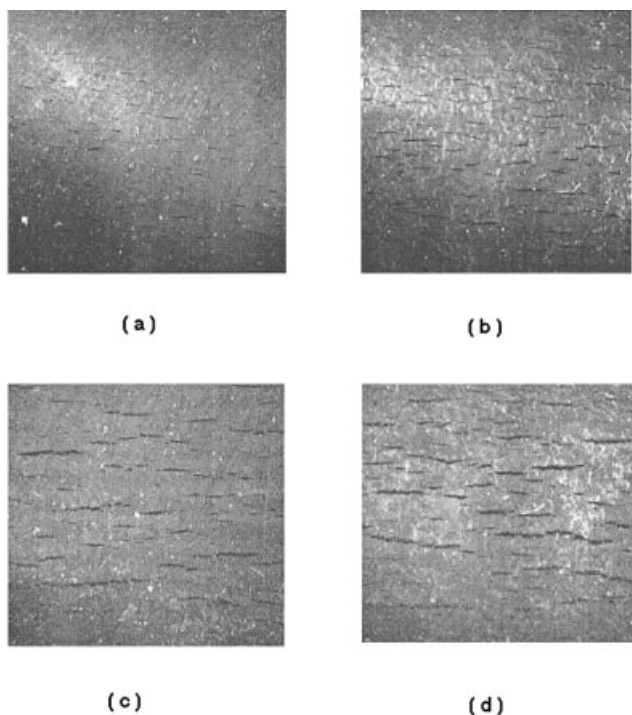**Figure 4** Effect of metal poisoning on air-aged abrasion properties.

TABLE V
Dynamic Mechanical Properties

Test parameter	Compound	
	Control	Experimental
Original tan δ value at 100°C	0.15	0.14
Aged tan δ value at 100°C	0.16	0.12

The copper ion accelerates the breakdown of the rubber through the oxidation and reduction of the hydroperoxide[13]:

$$Cu^{+} + ROOH \rightarrow Cu^{+2} + RO^{\bullet} + OH^{-}$$

$$Cu^{+2} + ROOH \rightarrow Cu^{+} + ROO^{\bullet} + H^{+}$$
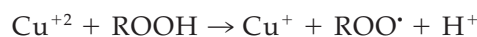
The immediate consequence is the rapid decrease of the effective chain length and also the mechanical property. The elongation at break of the experimental compound also decreased compared to that of the control compound as a result of excessive shortening

(a) Bent loop ozone tested control sample after 24 h at 20 X magnification
(b) Bent loop ozone tested experimental sample after 24 h at 20 X magnification
(c) Bent loop ozone tested control sample after 72 h at 20 X magnification
(d) Bent loop ozone tested experimental sample after 72 h at 20 X magnification

Figure 5 Effect of metal poisoning on ozone resistance in bent-loop mode: (a) bent-loop ozone tested control sample after 24 h at ×20 magnification; (b) bent-loop ozone tested experimental sample after 24 h at ×20 magnification; (c) bent-loop ozone tested control sample after 72 h at ×20 magnification; (d) bent-loop ozone tested experimental sample after 72 h at ×20 magnification.

Scheme 1

Figure 6 Effect of metal poisoning on anaerobic-aged swell index.
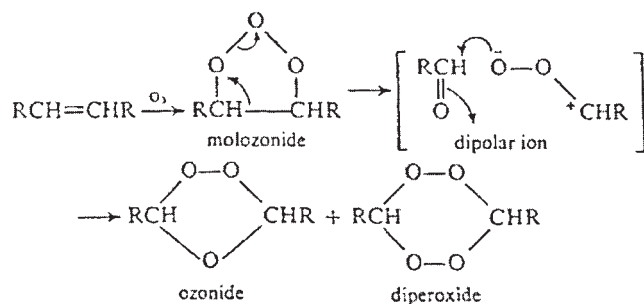
of chain length. The same was also observed in case of the oil-aged and anaerobic-aged samples.

The unaged and aged hardness, as shown in Figure 3(a,b), clearly indicated that the poisoned compound was softer compared to the control compound after ageing, which is in accordance with the explanation given earlier.

The unaged abrasion of both compounds was comparable, as shown in Figure 4. However, after ageing, the abrasion loss of the experimental compound was very high and is attributed to the softening of the experimental compound that results from ageing.
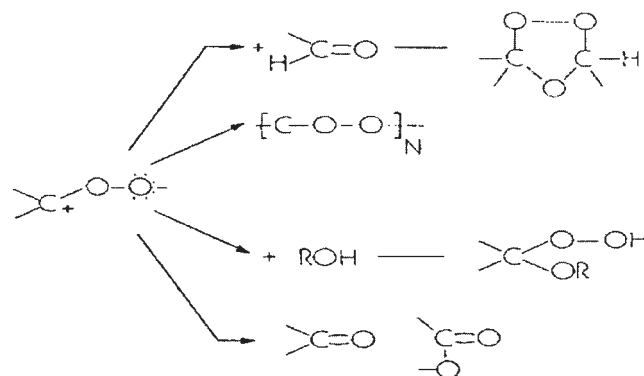
The dynamic mechanical property is shown in Table V.

The tan δ at 100°C, a relative indicator for the temperature buildup, was lower for the experimental compound.

The microphotographs of the bent-loop ozone samples, as shown in Figure 5, indicate that the experimental compound had higher numbers of cracks with greater depth than that of the control compound.

The probable mechanism[13,15] for ozone attack on the olefinic double bonds in natural rubber as shown in Scheme 1.
The ozonide formed in the ozonolysis process is oxidized or reduced to ketone, acid, aldehyde, and alcohol.[15] The intermediate dipolar ion can also be trans-
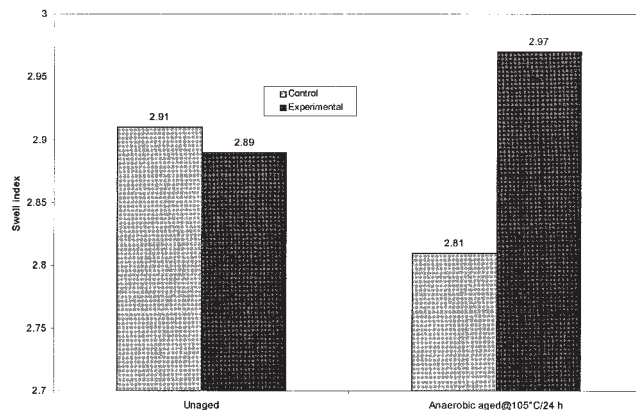
formed to ozonide, polyperoxide, hydroperoxide, and ketonic products, expressed as Scheme 2.[16]
The hydroperoxide formed will decompose at a faster rate in the presence of copper ion, as described earlier.

The swelling index and volume fraction of original (unaged) samples was comparable for both compounds. Nevertheless, after the anaerobic ageing, the swelling index and volume fraction of control compound decreased, as shown in Figures 6 and 7. The volume fraction of the experimental compound decreased substantially after ageing, resulting from the breakdown of the chains in the presence of metal poison as described earlier.

The storage stability of both green compounds under normal laboratory conditions, as shown in Figure 8, was comparable even after 150 days of storage.

After outdoor ageing of 90 days, the tensile properties (tensile strength and elongation at break) of the experimental compound was lower compared to those of the control compound, as shown in Figure 9.

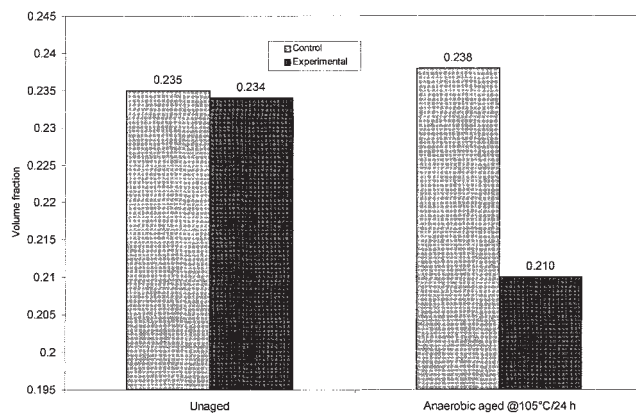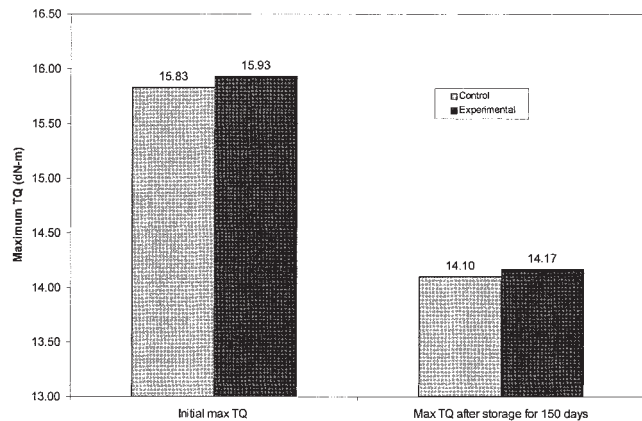Reaction kinetics of the metal poisoning of rubber compound was studied in accordance with an Arrhe-

Scheme 2

Figure 7 Effect of metal poisoning on anaerobic-aged volume fraction.

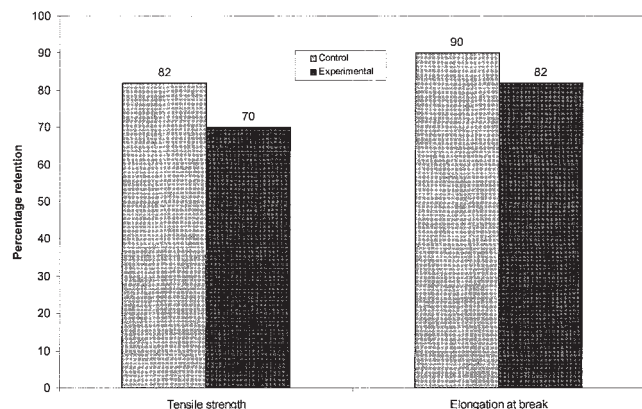**Figure 8** Effect of metal poisoning on storage stability of green compound under laboratory conditions.

Figure 10 Reaction kinetics of metal poisoning.

nius equation. The tensile strength was measured after 2, 4, and 6 weeks of ageing at 70°C. The rate equation expressed below was followed:
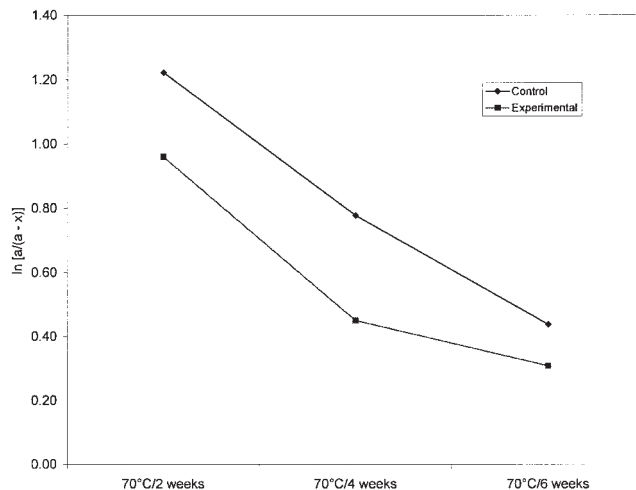
$$\ln a/(a - x) = kt$$

where a is the initial concentration of reactant, x is the concentration of the reactant after time t, and k is the rate constant. If the plot of $\ln a/(a - x)$ versus time t generates a straight line, then the reaction is considered to follow first-order reaction kinetics. The unaged tensile strength was considered as a and x is the tensile strength after 2, 4, and 6 weeks of ageing at 70°C. The generated curve was a straight line, which confirms the first-order reaction kinetics (Fig. 10).

From the slope of the curve, the rate constant of the degradation reaction was calculated and, using this rate constant, the half-life of both compounds was estimated using the following equation applicable for first-order reaction kinetics:

$$\text{Half-life } (t_{1/2}) = 0.693/k$$

The half-life of the control compound at 70°C was 23 days compared to 18 days for the experimental compound.

CONCLUSIONS

Under normal laboratory conditions, the storage stability of the green compound was scarcely affected by metal poisoning. However, the scorch safety of the experimental compound was substantially affected by metal poisoning. Hot-air ageing property, ozone resistance, outdoor ageing, and anaerobic-ageing property of the experimental compound were inferior compared to those of the control compound. The oil-aged tensile property was not significantly affected. After ageing the tan δ of the poisoned compound was lower and abrasion loss increased. The degradation kinetics of metal poisoning was a first-order reaction and the service life (as expressed by the half-life period) was drastically reduced for the poisoned compound.

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Figure 9 Effect of metal poisoning on percentage retention of physical properties after outdoor ageing of 90 days.

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