

Study of Cu–Zn–Co ternary alloy-coated steel cord in cobalt-free skim compound

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(Received 23 December 2013; final version received 5 March 2014; accepted 6 March 2014)

In this study, it is shown that the rate of bond degradation due to ageing in hot & humid conditions can be significantly reduced by the use of a Cu–Zn–Co ternary alloy coating, compared to current compounds and normal brass-coated steel cord. To better understand the adhesion mechanism, X-ray photoelectron spectroscopy is used to investigate the adhesion interface upon hot and humid ageing. In addition, the effect of removal of cobalt salts from compound on static and dynamic rubber compound properties is studied: it is found that this leads to improved heat ageing resistance, slower crack growth rate and less hysteresis. Hence, the new Cu–Zn–Co ternary alloy coating for steel cord allows cobalt salts to be removed from tires, which makes tires more durable and eco-friendly.

Keywords: steel cord; rubber; adhesion; interface; cobalt; XPS

Introduction

Brass-coated steel cords are extensively used as reinforcement material in radial tires, high-pressure hydraulic hoses and heavy-duty conveyor belts. The use of steel cords leads to improved strength, stiffness, stability and uniformity in tires.

The brass coating, electrolytically deposited on the steel surface, is in fact the bonding agent that provides strong and robust adhesion between the reinforcing element (steel cord) and the adjacent rubber compound (adhesion or skim compound). The mechanism of this bonding, involving the formation of a copper sulphide layer capable of physically bonding with rubber, was first introduced by Van Ooij.[1–3] In our previous publications, this bonding mechanism was reviewed, in addition with the function of the Cu_xS (here $1 \leq x \leq 2$), ZnS and ZnO interfacial layers in adhesion build-up and degradation.[3–6]

In order to have good adhesion formation and to reduce the rate of degradation of adhesion, particularly due to ageing in hot and humid conditions, cobalt salts are added to the rubber (skim) compounds that are in contact with the steel cords.[1–7] Van Ooij found the rate of dezincification, the mechanism that deteriorates the adhesion interface upon ageing, to decrease when cobalt salts are added to the skim compound. He proposed that cobalt ions diffuse into the ZnO layer and occupy its interstitials, which leads to the reduction of electrical conductivity of the ZnO layer. As a result, the presence of cobalt ions reduces the possibility of dezincification and increases the corrosion resistance of the adhesion interface in humid and salty environments.[1–3,7]

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However, cobalt is considered to be ‘poison’ for the rubber, since, like most transition metals, cobalt is an oxidation catalyst. In addition, cobalt is an expensive, strategic material. By adding cobalt randomly to the whole rubber compound, too much cobalt is used, since cobalt only has a beneficial functionality at the brass surface.

Bekaert has developed a new metallic coating for steel cord that allows removal of cobalt salts from the compounds: a Cu–Zn–Co ternary alloy coating, i.e. a brass alloy with some cobalt added, called TAWI (Ternary Alloy coating on Wire). Here, the adhesion performance of regular brass-coated steel cord in a cobalt-containing skim compound is compared with the Cu–Zn–Co ternary alloy coating in a cobalt-free compound. Furthermore, the same analytical approach as previously debriefed [4,5] is used to investigate the adhesion bond degradation mechanisms of steam ageing (SA): i.e. upon vulcanization with the filter paper method, the adhesion interface is characterized by X-ray photoelectron spectroscopy (XPS) depth profile analysis. In addition, the basic mechanical properties of both compounds are studied, as well as their respective degradation rate upon heat ageing (HA), their dynamic mechanical properties E' , E'' and $\tan \delta$, and their crack growth rate with the Coesfeld-Bayer Tear Analyser.

Experimental

The steel cord construction used in this investigation is 2×0.30 ST, with a brass coating with 63.5 wt% Cu + 36.5 wt% Zn, and a ternary alloy coating with 67 wt% Cu + 29 wt% Zn + 4 wt% Co, both with a coating weight of 3.6 g/kg. The coatings were applied on wires at intermediate diameter via sequential electroplating of Cu, Zn (and Co) and a thermal diffusion process to create the binary (ternary) alloy Cu–Zn(–Co). Then, the coated wires were drawn to 0.30-mm diameter and bunched into 2×0.30 ST cords.

The formulations of the compounds used in this investigation are given in Table 1. Adhesion testing was done according to ASTM D 2229-02 measuring with an Instron 5565 Tensile Tester, the force required to pull out the samples (= pull out force, POF (N)) and rating the rubber coverage (= appearance rating, APR (%)). And this with six repeats for each sample at each cure and ageing condition; here the respective average results of each are presented.

Table 1. Formulation (in phr, i.e. part per hundred rubber) of the 2 compounds used in this study.

	Compound with Co	Cobalt-free compound
TSR 10 (phr)	100	100
Carbon Black N326 (phr)	65	65
Zinc Oxide (phr)	9	9
Manobond 680C (phr)	1.2	
Stearic Acid (phr)		0.7
6PPD ^a (phr)	1.8	1.8
DCBS ^b (phr)	0.8	
TBBS ^c (phr)	6.4	0.7
Crystex HSOT20 (phr)		6.4
Santogard PVI (phr)		0.25

^aAnti-oxidant, *n*-(1,3-dimethylbutyl)-*n*'-phenyl-*p*-phenylenediamine.

^b*n,n*- dicyclohexyl-2-benzothiazole sulphonamide.

^c*n*-tert-butyl-2-benzothiazole sulphonamide.

For characterization of the adhesion interface, the steel cord samples were covered with a filter paper (Hardened Ashless Circle Filters of Whatman, Type 540, with particle retention in liquid of 8 μm), sandwiched between two uncured pads of rubber compounds, and then placed in a mould; this procedure was applied in our previous studies,[4,5] and by others.[8–10] Vulcanization was done with an Agila cure press and in a mould at 150 °C with controlled pressure (133 kN) and reduced flow. After curing (and respective ageing), samples for surface analysis of the adhesion interface were obtained by cutting open the rubber and removing the steel cord samples and by peeling away the filter paper. For steam-aged adhesion, test samples were put in a steam chamber at 120 °C (after initial curing for 25 min at 150 °C). For cured humidity ageing (CH) testing, vulcanized samples were put in a humidity chamber at 93 °C & 95% RH. For heat aged adhesion, vulcanized test samples were put in a heating furnace at 80 °C.

XPS data were acquired with a Thermo Scientific K-Alpha XPS. This system uses mono-chromatized Al-K α radiation ($h\nu = 1486.6\text{ eV}$) as the excitation source. The analyzer with a take-off angle of 45° was operated at constant pass energy of 23.50 eV. Depth profiling was performed using the Ar⁺ ion gun (2 keV) with a sputtering rate of $\pm 0.1\text{ nm/s}$ (for $\alpha\text{-Fe}$). The operating pressure during analysis was in the low 10^{-8} Torr range. All spectra were acquired with an X-ray spot of 100- μm diameter. The acquired regions were C 1s, O 1s, S 2p, Fe 3p, Cu 2p₃, Co 2p₃, Cu L3M45M45, Zn 2p₃ and Zn L3M45M45.

The rheometer curves were determined at 150 °C with a Monsanto MDR 2000E Moving Die Rheometer, provided by Alpha Technologies.

Dynamic mechanical properties (E' , E'' and $\tan \delta$) of the compounds were determined with an Eplexor 100 N, applying a temperature sweep -100 to $+100$ °C; 10 Hz and 2% dynamic deformation following ISO 4664-1:2005.

To study the dynamic crack growth rate of the two compounds, we decided to apply Coesfeld-Bayer Tear Analyser at DIK¹, as this test was shown to have excellent correlation with service performance of various tire components.[11]

Tests were carried out using a Fatigue Tear Analyser System manufactured by the Coesfeld-Bayer Companies. This system operates with 10 single-edge notch (SEN) specimens in tension. SEN-vulcanized rubber samples, $65 \times 15 \times 2\text{ mm}$ with initial crack length of 2 mm, were tested at tensile strain-controlled amplitude of 20, 25, 30 and 35%, in dynamic loading with 50-ms pulse, controlled temperature of 30 °C and test frequency of 10 Hz (test standard IEC 17025:2005).

Results and discussion

Adhesion performance & mechanism

In Figure 1, the POF adhesion results of brass-coated steel cord in cobalt-containing compound, brass-coated steel cord in cobalt-free compound and Cu–Zn–Co ternary alloy-coated steel cord in cobalt-free compound upon initial adhesion (RC), over curing (OC) and different accelerated ageing tests are plotted. In Figure 2, the rubber coverage (= appearance rating, APR) results of the same samples are plotted. Judging POF and APR together allows to make proper statement of the adhesion performance. Initial adhesion of the Cu–Zn–Co ternary alloy coating in cobalt-free compound is 12% lower than the reference system. Adhesion upon over cure of 400 min of all samples is similar to each other. APR of all samples is similar compared with initial adhesion, whereas POF values are significantly lower than upon RC. The latter can be explained by

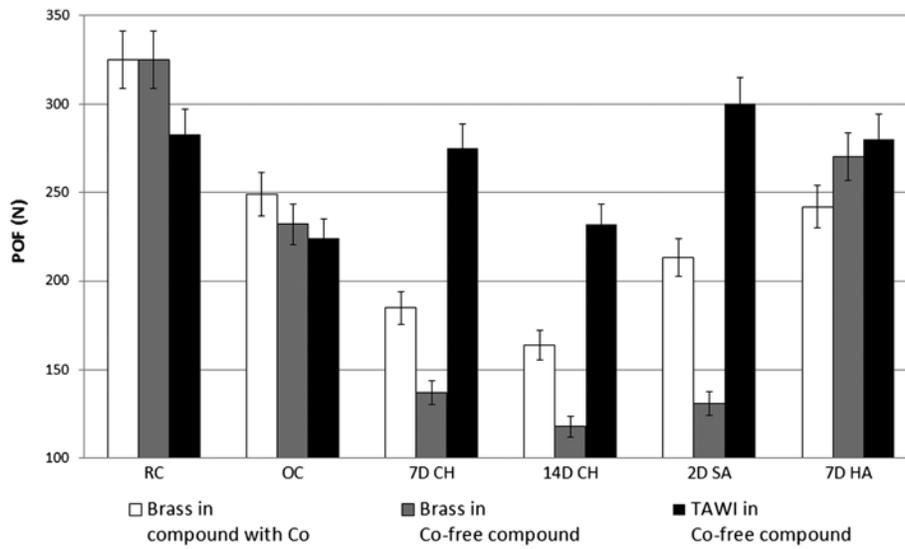


Figure 1. Average POF adhesion results of (1) Brass-coated steel cord in cobalt-containing compound, (2) Brass-coated steel cord in cobalt-free compound and (3) Cu–Zn–Co TAWI in cobalt-free compound upon RC & OC (25 min and 400 min cure at 150 °C), 7 and 14 days of CH, two-days SA and seven-days HA.

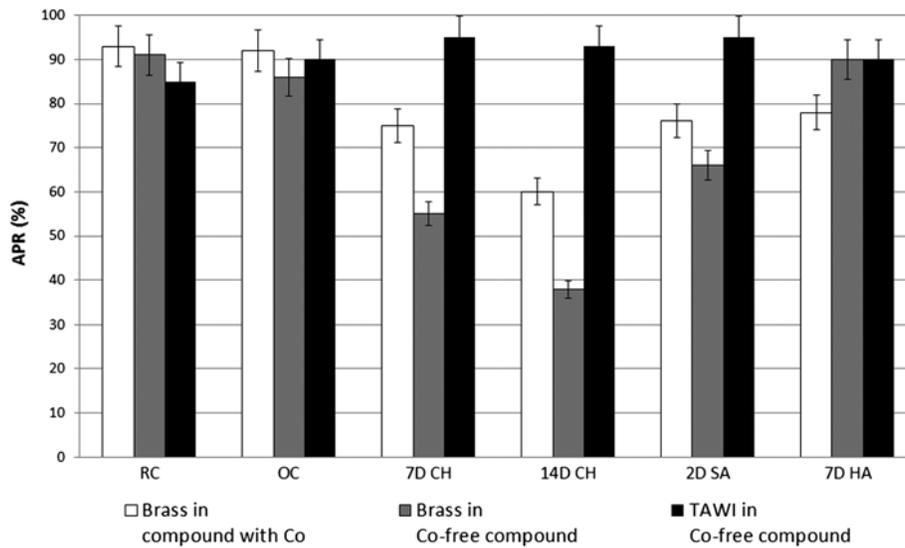


Figure 2. Average APR adhesion results of (1) Brass-coated steel cord in cobalt-containing compound, (2) Brass-coated steel cord in cobalt-free compound and (3) Cu–Zn–Co TAWI in cobalt-free compound upon RC & OC (25 min and 400 min cure at 150 °C), 7 and 14 days of CH, two-days SA and seven-days HA.

reversion of the compound. Adhesion results upon hot and humid ageing, i.e. both cured humidity and SA, are better for the Cu–Zn–Co ternary alloy coating in cobalt-free compound.

This improved adhesion retention can be attributed to the ternary alloy coating, as the results upon such ageing tests of brass-coated steel cord in cobalt-free compound are a lot inferior to both systems presented here, which demonstrates the retarding effect of cobalt on dezincification of brass or adhesion interface leading to slower adhesion degradation in hot & humid conditions, as shown in previous studies.[1–5,7]

In cobalt-free compound, brass and Cu–Zn–Co coating exhibits almost similar POF and APR upon heat-ageing conditions. This improved adhesion is probably due to absence of cobalt salts in the compound as heat-aged adhesion results for brass-coated steel cord in cobalt-free compound are equal to the results obtained with the Cu–Zn–Co ternary alloy coating. The brass and the ternary coating system show similar adhesion results after HA as in this ageing mechanism no excess of humidity and moisture is loaded on the system, thus the dezincification degradation mechanism of the interface is in general not expected to occur.

In order to study the mechanism of improved adhesion retention upon SA, XPS was used to characterize the respective adhesion interfaces as done in previous studies.[4,5,8–10] In Figure 3, a complete XPS depth profile, as published in earlier work,[4,5] of the Cu–Zn–Co ternary alloy coating in cobalt-free compound, upon curing and three-days SA is presented. The Cu and Zn LMM auger peaks were used, and deconvoluted, after non-linear least-square fitting analysis (NLLSF), in their respective substances present throughout the profile. In addition to the chemical interlayers of the interface (Cu_xS, ZnS and ZnO) and coating (Cu & Zn) that also can be observed with a regular brass-coated steel cord,[4,5] cobalt is present throughout the interface and

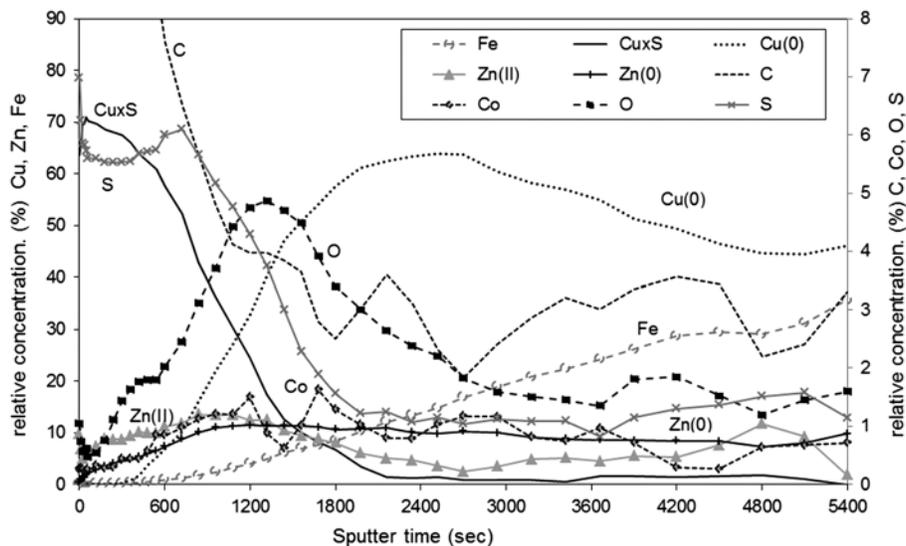


Figure 3. Chemical XPS depth profile of the adhesion interface of a Cu–Zn–Co TAWI in cobalt-free compound after three-days SA at 120 °C, obtained after NLLSF of the respective LMM Auger electron lines of Cu and Zn (cf. Cu & Zn LMM NLLS Factor01 and Factor02, resp. Cu_xS, Cu(0), Zn(II) and Zn(0)), as done in Buytaert et al.[5].

coating. The latter indicates that cobalt integrates into the Cu_xS – ZnO interface upon vulcanization and ageing. By study of the peak position of $\text{Co } 2p_3$ throughout the depth profile, the chemical nature of cobalt was investigated. Here, cobalt throughout the profile can be $\text{Co}(0)$ or cobalt sulphide; due to the low concentration of cobalt and the respective peak positions being close to each other, we were not able to conclude that no cobalt sulphide was formed.[12,13] Compared with a typical depth profile before SA,[4,5] it can also be noted that the interfacial interlayers, Cu_xS and ZnO , have significantly grown upon SA.

Figure 4 presents an overlay of the Cu_xS (with $1 \leq x \leq 2$) depth profiles of brass-coated steel cord in cobalt-containing compound, brass-coated steel cord in cobalt-free compound and the Cu – Zn – Co coating in cobalt-free compound, obtained after NLLSF analysis of the copper LMM auger lines. For all systems, the Cu_xS profiles are almost equal, which indicates that the thickness of the ‘dendritic’ sulphide layers is similar and does not immediately explain the difference in adhesion performance. In Figure 5, an overlay of the ‘ $\text{Zn}(\text{II})$ ’ (= $\text{ZnS} + \text{ZnO}$) depth profiles of the three systems is shown, obtained after NLLSF analysis on the zinc LMM lines. It can be seen that the $\text{Zn}(\text{II})$ -intermediate layer of the interface is substantially bigger for the brass-coated steel cord in cobalt-containing and cobalt-free compound. Compared with the typical thickness of this layer at initial adhesion curing, such as presented in,[4,5] this $\text{Zn}(\text{II})$ -intermediate layer for the brass-coated steel cord is also significantly grown upon SA, which is in-line with prior observations,[1,2,5–7] and is explained by dezincification as mechanism behind adhesion degradation during SA. A ternary alloy with few wt% cobalt added to brass exhibits much slower dezincification than normal brass; hence, cobalt inhibits to some extent the brass corrosion in hot and humid condition.

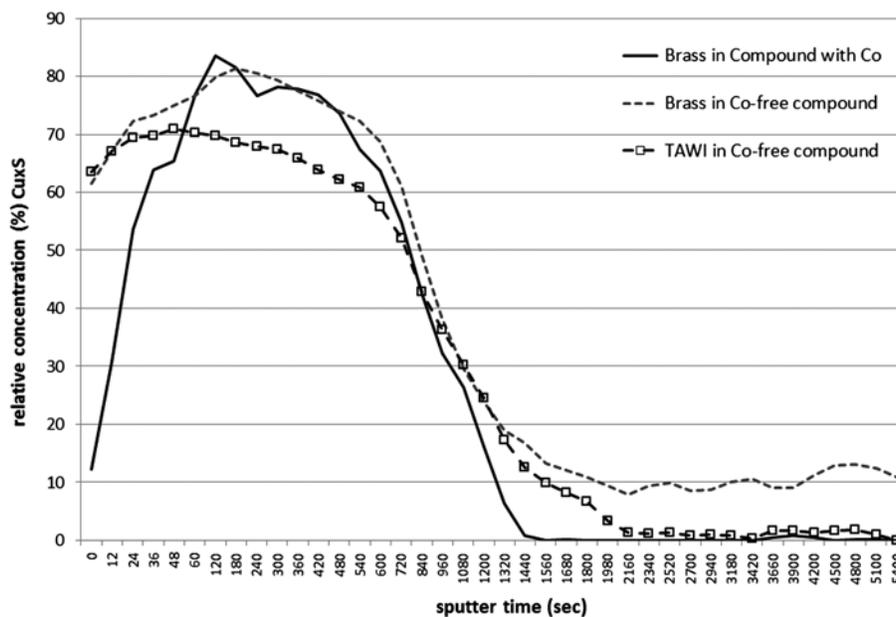


Figure 4. Overlay of Chemical XPS depth profiles of Cu_xS ($1 \leq x \leq 2$) of the adhesion interface obtained from NLLSF of the respective Auger electron line, as done in Buytaert et al.[5] of (1) Brass-coated steel cord in cobalt-containing compound, (2) Brass-coated steel cord in cobalt-free compound and (3) Cu – Zn – Co TAWI in cobalt-free compound after three-days SA at 120°C .

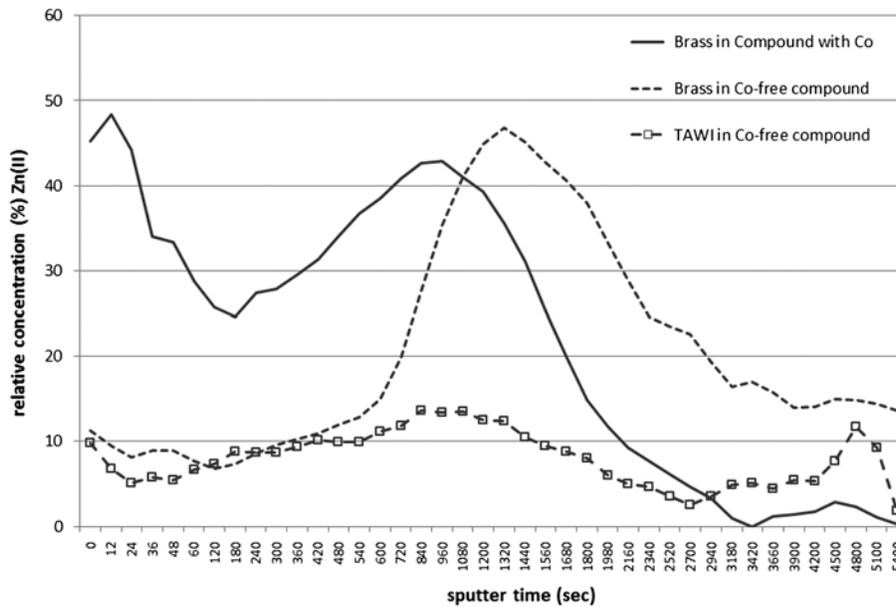


Figure 5. Overlay of Chemical XPS depth profiles of ZnO & ZnS (cf. Zn(II)) of the adhesion interface from NLSF of the respective Auger electron line, as done in Buytaert et al.[5] of (1) Brass-coated steel cord in cobalt-containing compound, (2) Brass-coated steel cord in cobalt-free compound and (3) Cu–Zn–Co TAWI in cobalt-free compound after three-days SA at 120 °C.

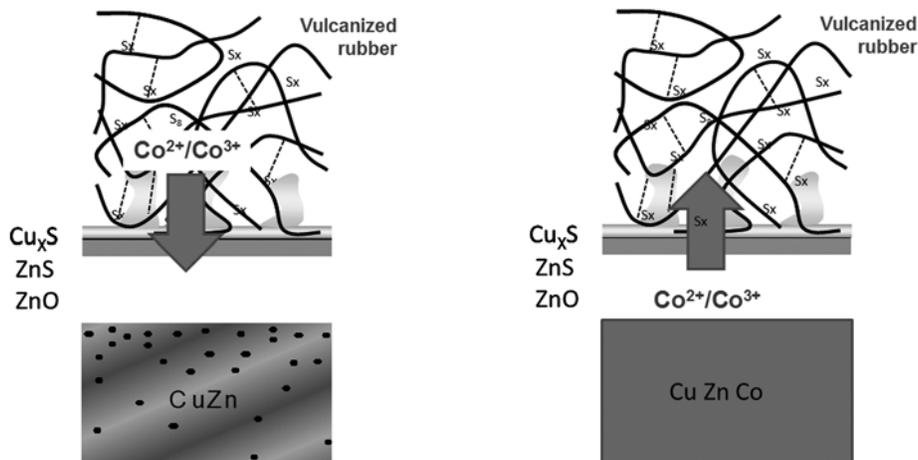


Figure 6. comparison of the adhesion mechanism of (1) Brass-coated steel cord in cobalt-containing compound and (2) Cu–Zn–Co TAWI in cobalt-free compound.

In Figure 6, a comparison is made of the adhesion mechanism of brass-coated steel cord in cobalt-containing compound, as known from van Ooij et al.[1–3], and Cu–Zn–Co ternary-coated steel cord (TAWI) in cobalt-free compound. In both cases, mechanical anchorage of the vulcanized rubber polymer network with and inside the

grown Cu_xS asperities (also called dendrites) is thought to explain mainly the adhesion between rubber and steel cord. Also the incorporation of cobalt inside the respective sulphide-oxide interfacial layers is highlighted. Incorporation of cobalt ions from the adjacent skim compound upon vulcanization was shown also by Fulton et al.,[7] and it is claimed that doping of the semi-conducting Cu_xS–ZnS–ZnO interlayers by cobalt explains the slower dezincification of the underlying brass coating, which results in longer adhesion retention in hot and humid ageing conditions. On the other hand, putting cobalt in the coating, where its function is required, instead of in the rubber compound, appears the most efficient solution for optimal adhesion performance, as cobalt incorporates more readily in the interfacial layers upon oxy-sulphidization of the coating metallic elements during compound vulcanization and adhesion build-up.

Compound mechanical properties

In Table 2, the main rheological properties at 150 °C of the two compounds are noted. Tc2 (Time to 2 lbf.in rise above minimum torque (ML)) of the cobalt-free compound is a little higher, this probably due to the addition of the amount of retarder, PVI. Tc90 (Time to 90% of torque increase) of both compounds are rather similar, which indicates the successful compensation for elimination of cobalt salt from the compound, by adding stearic acid and by changing accelerator from DCBS to TBBS. Maximum torque (MH), an indication of cross-link density of the vulcanized compound, is a little lower for the cobalt-free compound; this indicates that the increasing effect on crosslink density of cobalt salt addition to a compound is here not completely compensated for.

Table 3 shows the static mechanical properties of both compounds. Shore A hardness of both compounds is comparable. Tensile strength of the cobalt-free compound is higher, and the respective moduli are lower. Elongation at break (Eb) at initial cure is about 30% higher for the cobalt-free compound. Eb after five days of HA at 80 °C of both compounds is lower compared to initial cure state, due to oxidative ageing. Eb of the cobalt-free compound after HA is about 50% higher, which indicates a slower degradation of the compound upon HA, which probably can be explained by the absence of cobalt in the compound, as cobalt is regarded as an oxidative catalyst for rubber compounds. This improved durability of the cobalt-free compound (compared to the cobalt-containing compound) can, according to recent National Highway Traffic Safety Administration and Ford studies, lead to longer tire endurance.[14] In combination with the improved fatigue properties of this cobalt-free compound (see further), as well as the improved adhesion retention upon hot and humid ageing/service conditions when using a Cu–Zn–Co ternary alloy-coated steel cord, it can be expected that this can lead to a longer life-time of radial tires, and improved retreadability of truck and bus radial tires (TBR), which can give significant value to TBR end-users, the transportation companies.

Table 2. Rheometer properties of the 2 compounds used in this study.

	Compound with Co	Cobalt-free compound
Tc2 (min)	1.8	3.5
Tc90 (min)	12.0	13.0
MH (dNm)	31.5	30.6

Table 3. Static mechanical properties of the 2 compounds used in this study.

	Compound with Co	Cobalt-free compound
Shore A hardness	66	64
Tensile strength (N/mm ²)	19.5	25.0
Modulus 100% (N/mm ²)	3.85	3.2
Modulus 200% (N/mm ²)	9.3	7.8
Modulus 300% (N/mm ²)	15.7	13.6
Elongation at break (Eb - %)	365	480
E b (%) after 5 days HA at 80 °C	208	324

A comparison of dynamic crack propagation rate, for both compounds with increasing strain amplitudes, obtained with Coesfeld-Bayer Tear analyser, is plotted in Figure 7. The cobalt-free compound has lower crack growth rate and the difference increases with increasing strain amplitude. The cobalt-free compound has also a lower stress intensity factor (K) ahead of crack tip (i.e. the cobalt-free compound is 'tougher'). These test results are consistent with earlier obtained DeMattia results, in which the cobalt-free compound also exhibited a slower crack growth rate. The better crack growth rate of the cobalt-free compound can be due to a longer network chain length or low cross-link density, which also the difference in MH in the rheometer (see Table 2 MH) seems to indicate. However, the respective network chain length of both compounds still has to be determined, e.g. by solvent-swelling method.

In Table 4, dynamic mechanical properties, measured at 60 °C, 10 Hz and 2% dynamic deformation of both compounds are listed. The test conditions were chosen to reflect operating temperature and conditions of tire application.[15] The storage modulus E' , the loss modulus E'' and $\tan \delta$ of the cobalt-free compound are significantly lower. The respective ~30% lower $\tan \delta$ and ~50% lower E'' can lead to small, but significant, reduction in rolling resistance of tires when going from cobalt-containing to cobalt-free skim compound.

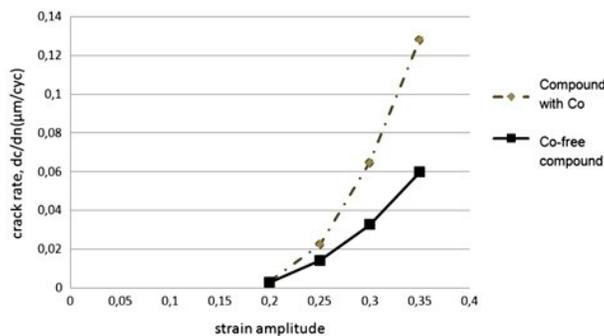


Figure 7. Dynamic crack propagation rate of both compounds with increasing strain amplitudes.

Table 4. Dynamic mechanical properties of the 2 compounds used in this study, measured at 60 °C, 10 Hz, 2% dynamic strain.

	Compound with Co	Cobalt-free compound
E' [MPa]	12.61	8.58
E'' [MPa]	1.98	0.94
Tan δ [-]	0.157	0.109

Conclusions

In this study, it has been shown that a Cu–Zn–Co ternary alloy coating in combination with cobalt-free tire compounds leads to several advantages:

- improved adhesion retention in hot and humid conditions,
- slower oxidative HA,
- slower crack growth rate and
- less hysteresis.

Hence, a Cu–Zn–Co ternary alloy, with few wt% cobalt added to brass, allows removal of cobalt salts from the skim compounds in tires and can bring several advantages, such as longer life-time of TBR tires. Less hysteresis indicates a potential reduction of rolling resistance of tires, which can lead to lower fuel consumption, less CO₂ and improved local air quality. Removal of cobalt salts as a compound ingredient also improves the ecological performance of tire plants.

A filter paper – XPS study has demonstrated that the Cu–Zn–Co ternary alloy exhibits much slower dezincification than normal brass upon SA. Putting cobalt in the coating/interface, where its function is required, instead of in the rubber compound, appears the most efficient solution for optimal adhesion performance.

Note

1. DIK = Deutsches Institut für Kautschuktechnologie = German Institute of Rubber Technology.

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