Effect of Sn on the Adhesion between Cu–Sn Alloy Coated Steel and Styrene Butadiene Based Rubber

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The effect of Cu–Sn coating on steel towards improving the adhesion between steel and typical styrene butadiene rubber (SBR) based tyre bead composition has been investigated in this work. Steel coupons were coated with varying compositions of Cu–Sn via immersion coating, where the electrolyte bath composition was varied. Chemical analysis of the coatings using ICP-OES confirmed increase in Sn content with increasing SnSO4 concentration in the coating baths, keeping other parameters constant. No change in the surface roughness and coating weight was observed with change in Sn concentration in the coatings. The coated steel plates were vulcanized with SBR based rubber and peel strength was measured. The results confirmed an optimum Sn concentration of 3–4 wt% in the coatings up to which an increase (~ 25%) in adhesion strength was exhibited compared to only Cu coatings. Stereo-microscopic analysis of the peel tested samples validated mixed mode i.e. both adhesive and cohesive modes of failure.

KEY WORDS: Cu–Sn coating; steel substrate; bead rubber; vulcanization; peel strength.

1. Introduction

Rubber composites with high strength steel wires as reinforcing elements are widely used in a variety of products, including conveyor belts, heavy duty hoses, pulley belts, pneumatic and radial tyres. In today’s tyre technology, steel wires are bonded together with rubber to form a composite structure to enhance tyre’s structural support and mechanical stability. In order to dissipate stress and to bear the load on the tyre during its service life, the interface between steel and rubber plays the most crucial role like all other composite structures. Therefore, proper adhesion of the steel wire with rubber is of prime importance and a widely researched topic. Adhesion between steel and rubber takes place during the vulcanization/curing process of the green tyre which provides the interfacial strength. In the case of wire adhesion, chemical/electrochemical bond formation is of prime importance, as reported by researchers.1,2) Bonding agents or primers are applied on the pristine steel surface for bonding with rubber through curing process.2) Different kinds of coatings, their deposition methods and various surface treatments have been proposed in patent applications to improve the adhesion strength between rubber and steel wire.2)–11) Generally, copper (Cu) or copper based binary or ternary alloy coatings are most popular for this purpose. Copper - zinc (brass) coating has been already established for industrial applications as carcass of tyres, popularly known as steel tyre cord. A detailed review article by Van Ooij reported the bonding mechanism, adhesion model, role of different additives in rubber, effect of aging at interface bonding, different metal surface pretreatments and advanced ternary coatings like Cu–Zn–Co/Ni on steel wire.12) Other than tyre cords, steel wires in the form of strands are also used as reinforcement in the bead portion of the tyre which is termed as bead wires. Steel bead wires are coated with Cu or Cu based alloy, primarily Cu–Sn.13–15) One patent describes the method for manufacturing bead wire by electroless plating method which includes bronze with 2–30 wt.% tin.15) According to Van Ooij, the coating on steel wire reacts with sulfur which is added as a curing agent in rubber and forms an interfacial layer predominantly consisting of sulfide. This sulfide layer facilitates the adhesion of bead wire by mechanical and/or chemical interaction with the cured rubber. The coating composition of the steel wire has to be optimized to support the very specific requirements of the sulfide layer formation synergizing with the curing cycle of the rubber. Coating composition and the curing cycle need to be synchronized considering the delicate kinetics to achieve the optimum size and structure of the sulfide layer.16)

Stout et al. reported first the feasibility of producing industrial quality Cu–Sn coating in laboratory through displacement plating.13) They used water based sulfate bath of Cu, Sn and Fe in acidic condition to deposit Cu–Sn coating on flat steel coupons. Coating thickness was varied by altering the immersion time between 1–10 seconds and as a result the thickness varied between 60–190 nanometers. An immersion time of 2 seconds closely reproduced the production line conditions. Sn concentration in coating was varied between 0–7 weight% by altering the Sn and Fe concentrations in bath. These samples were vulcanized with a typical bead rubber formulation and then peeled off the rubber layer.

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from steel surface. The peeled surfaces were characterized through auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) to understand the type of interfacial bond formed for varying Sn weight% in coating. However, it has not reported the adhesion strength values for different coating composition.

Cho et al. deposited thin film (30–90 nm) of copper on uniform surface of zinc-plated steel wires by the substitution/displacement coating route. The adhesion properties were reported to be a function of the coating thickness and copper film of 30 nm on average exhibited similar adhesion strength to the rubber compound compared with brass plated steel cords. The author reported that suppression of the excessive growth of copper sulfide on the copper-coated cord, due to the low copper coating thickness resulted in better adhesion at interface. Cho et al. in another paper reported the findings with different thicknesses of copper film varied between 30 to 90 nm on steel plate. The copper-coated plate containing an amount of copper coating sufficient to plate the surface with a uniform copper layer showed better adhesion than that having a small amount of copper coating on its surface. Good adhesion to the copper-coated plate was obtained when the rubber compound contained resinous bonding additives, and when either a normal or over-cured condition was employed. The high adhesion between the copper-coated plate and the rubber compound was ascribed to the sufficient formation of copper sulfide, when the modulus of the rubber layer was high enough to hold strongly to copper sulfide.

A patent disclosed bronze coating would provide good adhesion with bead rubber but claimed a wide range in Sn wt% (2–30) in the coating. However, very limited study on these aspects has been reported so far in literature. Therefore, the current work was aimed to find out a narrow range of coating chemistry and corresponding plating bath composition which can be used for industrial scale production. In the present work, Cu–Sn coatings with varying Sn wt% were deposited on steel plates via immersion route. The effect of variation in Sn weight% on the steel-rubber adhesion has been investigated by various compositional analysis techniques (i.e. SEM, EPMA) and peel test.

2. Experimental Procedure

2.1. Coating Synthesis

The Cu–Sn coatings were deposited on mild steel coupons of 2 mm thickness via immersion route. 20×20 sqmm size samples were used for coating characterization and 150×25 sqmm samples were used for the peel off adhesion test. All the plate samples were polished up to standard 600 grit polishing paper to reproduce the surface roughness of bead wires, which are generated after finish drawing at production line. Samples were cleaned with soap solution, running water and alcohol in sequence and finally dried with tissue paper. Immersion time was kept at 2 seconds. The established bath compositions of the commercial line in terms of copper sulfate (CuSO4, 35 g/l) and sulfuric acid (H2SO4, 40 g/l) concentrations were taken as benchmark during the study to meet the requirement of coating thickness (0.3–0.6 g/kg). Only the tin sulfate (SnSO4) concentration in the bath was changed as 0.11 g/l, 0.25 g/l, 0.50 g/l, 0.75 g/l and 1.00 g/l to vary Sn weight% in the deposited coatings.

2.2. Characterization

Coating composition analysis and surface coverage with coating were studied through Electron Probe Micro Analyser (EPMA, Cameca SX100) and Scanning Electron Microscope (JEOL JXA6400) coupled with Energy Dispersion Spectroscopy Analyser (EDS; Thermo Noran, USA). Bulk coating composition was determined from the flat samples after dissolving the coating as described by Mandal et al.19 and measured through inductively coupled plasma optical emission spectroscopy (ICP-OES; SPECTRO ARCOS ICP-OES Spectrometer; SPECTRO Analytical Instruments, Germany). Surface roughness of the flat samples before and after coating was measured through roughness profilometer (Veeco Dektak - 150). Coating weight in terms of gram/square meter (g/m²) was determined by the standard method of dissolving the coating in stripping solution containing 30 ml NH3 solution and 5 ml H2O2.

2.3. Measurement of Adhesion Strength

Adhesion strength was measured in terms of peel test. A typical SBR based bead rubber formulation was prepared in laboratory and the same was used for conducting the peel off test. Table 1 shows the rubber formulation used for the adhesion test experiments. 50×25 sqmm area of the plates prepared for adhesion test was coated in laboratory. It was vulcanized with 2 mm thick rubber pad made out of the laboratory bead rubber formulation from one side. The coated plate along with the rubber pad was cured at 150°C temperature under 13 MPa pressure in a curing press. Curing was continued for 3 min longer than the t90 time i.e. the time required to achieve 90% cured stage of the rubber formulation as obtained from the rheometric study (Oscillating Disc Rheometer, Monsanto Rheometer; R-100S complied with ASTM D 2084-95 standard) of the formulation to compensate for heat transfer. During the peel off adhesion test conducted in a tensile tester (Universal Testing Machine-1445;
Zwick GmbH & Co. Ulm, Germany), the force vs. displacement data was continuously recorded while peeling at 180° with crosshead speed of 100 mm/min. The rubber coverage, which was the relative extent of rubber, remained on the surface of the plate after the test was studied under stereo microscope to determine the mode of failure at interface. Peel strength reported for different coating compositions was derived from the average of three repeat tests.

3. Results and Discussion

3.1. Effect of Sn Concentration Increase in Bath on the Surface Roughness and Weight of the Deposited Coatings

The surface roughness ($R_a$ in μm) of the coatings deposited by varying the SnSO$_4$ concentration, while keeping the concentration of CuSO$_4$ and H$_2$SO$_4$ constant in the immersion coating bath, is reported in Fig. 1. Surface roughness is important for mechanical interlocking between rubber and steel during the vulcanization process. Rubber can flow inside the grooves present on a rough solid surface prior to curing and solidify which improve adhesion at interface. Initial surface roughness of the plates were kept higher (10 micrometer) to replicate drawn wire surface roughness. It is observed from Fig. 1 that the surface roughness after coating remained almost same. No change in roughness was observed with varying Sn content in the coating. Thin layer of coating (few hundred nanometers) is obtained in immersion coating technique. Therefore, the thin layer of coating (~ 90 nanometer) as obtained through immersion technique could not alter the highly rough (10 micrometer) surface profile of the bare substrate. Surface roughness as reported in Fig. 1 was independent of coating composition because the coating weight did not change with variation in Sn wt% in coating as reported in Fig. 2. Figure 2 shows the coating weight in plate for different SnSO$_4$ concentrations in plating bath. Overall coating weight was observed as 0.2 g/m$^2$ and did not change with increase in bath SnSO$_4$ concentration. SnSO$_4$ was the minor constituent in the plating bath. The coating efficiency was controlled by the CuSO$_4$ concentration and bath pH (H$_2$SO$_4$ concentration). As the major constituents of the plating bath (CuSO$_4$ and H$_2$SO$_4$) were kept same in all the experiments, the coating weight did not change with change in SnSO$_4$ concentration. Ping et al. also reported the similar trend in their experiments with SnSO$_4$ as major constituents and CuSO$_4$ as minor constituents in the plating bath.

3.2. Coating Composition and Surface Coverage with Sn Concentration Increase in Plating Bath

Bulk coating compositions for the various coatings was analyzed through ICP OES and the results are reported in Fig. 1. Effect of the SnSO$_4$ content in immersion coating bath on the surface roughness, showing no change in bare plate roughness after coating with various SnSO$_4$ in bath.

![Fig. 1](image1.png)

Fig. 1. Effect of the SnSO$_4$ content in immersion coating bath on the surface roughness, showing no change in bare plate roughness after coating with various SnSO$_4$ in bath.

![Fig. 2](image2.png)

Fig. 2. Effect of the SnSO$_4$ content in the plating bath on the coating weight and coating composition, showing no appreciable change in the overall coating weight but increase in Sn wt% in coating with increasing SnSO$_4$ concentration, while keeping the concentration of CuSO$_4$ (35 g/l) and H$_2$SO$_4$ (40 g/l) constant in the immersion coating baths.

![Fig. 3](image3.png)

Fig. 3. Elemental mapping through EPMA for Cu, Sn, O and S at surface for Cu-5 wt% Sn coated steel plate, showing uniform coating with Cu, Sn with presence of bare spots at locations with presence of O. (Online version in color.)
Fig. 2. It is noticed that the Sn content in the coating increased from 3 to 6.5 wt% (rest Cu) as the SnSO₄ content in the electrolyte bath was varied from 0.11 to 1.00 g/l. Sn wt% in the various coatings has been used for nomenclature of the samples in rest of the paper. Elemental mapping of the coated surface was conducted through EPMA. Element concentrations were mapped over an area on the surface against different color code where red depicts highest concentration, blue means no presence of the element and green means uniform average concentration at the selected location. One typical elemental mapping for the steel plate coated with 0.50 g/l SnSO₄ (with fixed CuSO₄ and H₂SO₄) in plating bath is shown in Fig. 3. It can be observed that the surface of the steel substrate was coated with Cu and Sn at locations along with presence of uncoated spots depicted by presence of oxygen (O) and sulfur (S) with no Cu. Higher magnification view of the surface under SEM and EDS analysis is shown in Fig. 4. Presence of covered (white contrast) and bare locations (grey contrast regions) can be observed clearly on the surface in Fig. 4. Corresponding point EDS analysis of the location covered with coating (EDS spectrum of point 1, Fig. 4(b)) revealed prominent peak of Cu, whereas, bare spots (EDS spectrum of point 2, Fig. 4(c)) showed prominent peaks for O and S with lower intensity peak of Cu. The peaks for Fe and Mn as appeared in both the EDS spectrums came from the substrate background. Simultaneous presence of O and S at the bare spots indicates formation of Fe sulfate due to reaction with the sulfate ion present in the plating bath. Uncoated spots present on the steel surface are attributed to the non-uniform coating deposition. As mentioned in the “Experimental procedure” section that the coating deposition was carried out for 2 sec only, which was not enough to form a thick coating with complete surface coverage. It should also be noted here that the steel samples were polished up to standard 600 grit polishing paper to reproduce the surface roughness of bead wires, which are generated after finish drawing at production line. Also, the non-uniformity of the coatings could be attributed to the self-limiting nature of the immersion coating technique. Presence of uncoated spots at surface after immersion coating was also reported by Stout et al. and Cho et al. As Fe does not react with sulfur, the bare spots at surface do not adhere to rubber due to lack of chemical bond formation. The problem of bare spots in case of immersion coating of highly rough surface was addressed by forming multilayer coatings. This issue has been discussed in detail in section 3.3 while discussing the peel test results.

3.3. Effect of Coating Composition on Adhesion Strength

The adhesion strength between the vulcanized SBR rubber and the Cu–Sn coated steel plates were estimated by carrying out peel test. Peel strength for a particular sample was determined by the standard method of taking an average force from the horizontal part of the peel force (N) vs. displacement (mm) graph after discarding 20% data from initial and end part of the graph. Adhesion strength for a particular coating composition was determined by taking an average of three samples. Average adhesion strength along with standard deviation for different Sn wt% in coating is reported in Fig. 5. It is observed that Cu–Sn coated samples revealed higher adhesion strength than that of Cu coated sample. It has been claimed in few patents that Cu–Sn coating increases the adhesion strength and provides better adhesion stability with rubber compared to only Cu coating, but the actual mechanism is being currently investigated in details. Highest interfacial adhesion strength was obtained for 3 to 4 wt% Sn in coating. Adhesion strength dropped with further increase in Sn content in coating. Drop in adhesion strength beyond 4 wt% Sn as obtained in the current study is due to higher amount of Sn enriched residue left on rubber side of the fracture surface after peel test as reported by Stout et al. They reported higher amount of coating residue obtained for 7 wt% Sn sample compared to 2 wt% Sn. AES analysis of the coating residue confirmed Sn enrichment as high as 100% in this coating residue. The source of the Sn enriched residue was attributed towards the entrapment of Sn oxide from the plating bath. Increase in SnSO₄ content in plating bath enhances the chance of Sn oxide formation and subsequent entrapment in the coating.

Photographs of the fracture surfaces (steel plate side and rubber side) captured through stereo-microscope are shown in Fig. 6 for different Sn content. Mixed i.e. adhesive-cohesive modes of fracture were observed in all the samples. At certain locations, failure happened within the rubber layer
(cohesive failure) with clear presence of rubber adhering to the steel plate. On the other hand, the fracture occurred along steel plate-coating interface causing adhesive mode of failure at another location. The failure from steel-coating interface (adhesive rupture) is explained schematically with the insert used within Fig. 6(c). Here the coating layer was clearly visible on the rubber side of the fracture surface with steel surface exposed at the plate side. Stout et al. also reported such mixed mode of failure with the presence of coating residue on rubber side of the fracture surface obtained after peel test for 0–7 Sn wt% coating.

3 wt% Sn coated samples showed similar failure pattern without any predominance mode between adhesive or cohesive fracture as depicted in Figs. 6(a) and 6(b) though the average peel force for 3 wt% Sn coated sample was higher than the Cu coated sample as shown in Fig. 5. Predominantly cohesive mode of fracture was observed in 5 wt% Sn coated sample (Fig. 6(c)) but average peel force was marginally lower than the 3 wt% Sn coated sample.

Mode of fracture of the different coating compositions at peel test could be corroborated with the variation of the peel force as shown in Fig. 7. The figure shows the variation in peel force across the complete cross section of the sample as monitored online during the testing. Large variation in peel force is typical for stick-slip mode of failure which leads to mixed mode of fracture at interface. Such mixed mode of fracture without any predominance between adhesive and cohesive rupture was observed for Cu and 3 wt% Sn coated samples. The force variation was comparatively lower in case of 5 wt% Sn coated sample which revealed predominantly cohesive mode of fracture. 6.5 wt% Sn coated sample again revealed large variation in force during peel test.

Peel force fluctuation occurs due to the fact that the required force for cohesive rupture is different than that of adhesive rupture. Chemical reaction between Cu and sulfur at interface takes place during vulcanization which forms Cu-sulfide and provides the interfacial adhesion strength. Formation of uniform Cu sulfide at interface ensure cohesive mode of fracture. Mixed mode of fracture occurred due to non uniform sulfide layer formation at interface leading to intermittent bonding between coating and rubber. Sulfide layer does not form at the bare spots because Fe does not react with sulfur to form any chemical bond. Presence of such bare spots was observed in the EPMA study (Fig. 3) and further confirmed through higher magnification SEM and EDS study results (Fig. 4), shown and discussed earlier in this paper. Cho et al. in their corresponding papers also reported the presence of such bare spots in plate and wire samples due to high surface roughness (~10 micrometer) of the bare substrate and thin layer of coating (~90 nanometer) as obtained through immersion technique could not cover
the rough substrate uniformly causing the presence of uncoated/bare spots at surface.  

4. Conclusions

Steel plates were successfully coated with varying compositions of Cu–Sn via immersion coating with controlled deposition kinetics and then were vulcanized with SBR based rubber. Sn content in the Cu–Sn coatings could be varied from 3–6.5 weight% by varying the SnSO$_4$ content and keeping the CuSO$_4$ and H$_2$SO$_4$ content unaltered in the electrolyte bath. Variation in Sn wt% in the Cu–Sn coatings did not show any change in the coating weight and coating roughness. The coated surface contained bare spots at locations with presence of oxygen as measured through EPMA. The adhesion strength between the coated steel plates and vulcanized rubber measured through peel test showed improvement in Cu–Sn coated samples compared to that in only Cu coated samples. Peel test results showed maximum interfacial adhesion strength for 3–4 wt% Sn in coating and the strength dropped with further increase in Sn content. Mixed mode i.e. adhesive and cohesive mode of interfacial fracture was observed with stick – slip mode of failure for Cu and Cu – 3 wt% Sn coated samples. The failure mode further indicated the presence of bare spots on the surface, attributed to high initial surface roughness and thin coating layer.

REFERENCES