ABSTRACT

In the present study, first ever attempt has been made to engineer steel surface through a novel Cu-Sn alloy coating deposited via immersion coating technique to improve interfacial adhesion between rubber and steel. There is a recent trend in employing steel reinforcements in rubber and such rubber-steel composites are widely used in a variety of products, including conveyor belts, heavy duty hoses, pulley belts, pneumatic and radial tires to enhance structural support and mechanical stability. Interfacial adhesion between steel and rubber is of prime importance and a widely researched topic to enhance service life of these products. The steel surface is conventionally coated with copper (Cu) to improve adhesion with rubber. However, it has remained as an ever-existing problem to achieve good interfacial adhesion because of the high affinity of Cu for sulfur, causing excessive growth of the interface layer during vulcanization with the sulfur cured rubber and depletion of sulfur from the adjacent rubber layer leading to lower modulus resulting lower adhesion strength. Cu based alloy coatings can help in improving the interface adhesion by restricting the excessive growth of the Cu-sulfide layer through controlling the availability of elemental Cu at interface during vulcanization reaction.

High strength steel wires are used as reinforcements in carcass and bead portion of the radial tires, and are termed as tire cord and tire bead wires, respectively. Copper-zinc (Cu-Zn) alloy coating is widely adopted technique industrially for tire cord wires, whereas bead wires are conventionally coated with Cu. In the current work, steel substrates were coated with varying compositions of Cu-Sn alloy via immersion coating and investigated for interfacial adhesion after vulcanization with styrene butadiene (SBR)

based tire bead rubber formulation. Chemical analysis of the coatings confirmed increase in Sn content with increasing $SnSO_4$ 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 peel strength of the vulcanized coated steel plates insinuate higher (~ 25%) interfacial adhesion strength for Cu-Sn coated samples compared to that for pure Cu coated samples, with an optimum adhesion strength for the coatings containing 3-4 wt% Sn.

Microstructural evolution in Cu-Sn coatings with varying Sn content (3-6.5 wt%) were studied to understand its effect on interfacial adhesion with SBR rubber. The phase formation prediction in different Cu-Sn alloy systems from Pourbaix diagrams constructed using FactSage revealed formation of higher amount of SnO_2 with increase in Sn content in the coatings. Quantitative depth profiling by glow discharge optical emission spectroscopy (GDOES), microstructural characterization by transmission electron microscopy (TEM) and phase analysis by grazing incidence X-ray diffraction (GI-XRD) confirmed presence of Cu_3Sn precipitates with increasing volume fraction as Sn content in coatings increases. Formation of Cu_3Sn precipitate and SnO_2 layer played crucial role in controlling the Cu activity at the coating-rubber interface to form optimally thick Cu-sulfide layer in Cu-Sn coating with 3-4 wt% Sn and thus provided the maximum adhesion strength.

The Cu-Sn alloy coated steel samples exhibited improvement in interfacial adhesion strength compared to pure Cu coating but showed mixed mode i.e. adhesive and cohesive mode of interfacial fracture with large variation in peel force indicating stick-slip mode of failure at interface. The coated surfaces exhibited bare spots or deep roughness trough as micro-discontinuities in the coatings, where formation of Fe_2O_3 was evident from scanning electron microscope (SEM) coupled with energy dispersive spectroscope (EDS), auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) analysis. Microstructural study of the coating cross-section and coating-substrate interface by TEM revealed inadequate penetration of coating inside these troughs.

In order to improve the adhesion further between steel and rubber, a novel coating deposition technique was developed, where a thin Cu strike layer followed by a Cu-Sn layer with varying Sn composition was deposited by immersion route. A comparative assessment of such double layer coating with single layer Cu-Sn coating in terms of coating morphology, surface coverage, coating-substrate interface and coating composition studied using laser confocal microscope (OLS), SEM-EDS, GDOES, XPS and TEM revealed improvement in surface coverage in the case of double layer coatings due to more uniform coating deposition with sufficient coating penetration inside the deep roughness troughs resulting in compact and micro-porosity free interface. Better adhesion strength with less variation in peel force and cohesive mode of fracture within the rubber was observed for the double layer coated samples. Pull out tests further conducted to measure the adhesion properties of the drawn wire samples with bead rubber showed an improvement of around 100 N pull out force over the maximum force obtained with single layer Cu-Sn coating.

Keywords: Cu-Sn coating; steel substrate; strike coating; coating coverage; coating-substrate interface; adhesion, bead rubber; vulcanization; peel strength; microstructure; Pourbaix diagram; intermetallic precipitate; SnO_2 layer