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RUBBER-TO-BRASS ADHESION IN STEEL TIRE CORDS: MECHANISMS AND INTERFACIAL ENGINEERING

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The article presents formation mechanism and evolution of the adhesion layer, as well as the design strategy for high-performance steel cord adhesion systems. It is shown that during vulcanization, ZnS forms primarily on the brass surface; however, due to its dense and brittle nature, its direct adhesive strength is low. Subsequently, non-stoichiometric, porous, acicular Cu₂S grows into the rubber matrix, creating a mechanical interlock with the vulcanizate. It is hypothesized that C=C double bonds in the rubber molecules can form covalent C–S bonds with the Cu₂S surface. Thus, chemical bonding and physical interlocking serve as the dual sources of adhesion. Cobalt salts modify the electrochemical state of the interface by incorporating into the ZnO lattice, thereby suppressing excessive ZnS formation and promoting Cu₂S growth. Resorcinol-formaldehyde resin migrates to the interface during vulcanization and forms a gradient network that provides physical anchoring, barrier protection, and load cushioning for the tire.

Keywords: steel tire cord, brass coating, adhesion mechanism, cobalt salt.

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АДГЕЗИЯ РЕЗИНЫ И ЛАТУНИ В СТАЛЬНЫХ КОРДАХ ШИН: МЕХАНИЗМЫ И ПРОФИЛИРОВАНИЕ ПОВЕРХНОСТЕЙ

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Приведены механизм формирования и эволюция адгезионного слоя, стратегия проектирования высокоэффективных систем адгезии из стального корда. Показано, что во время вулканизации ZnS образуется преимущественно на поверхности латуни, однако, поскольку он плотный и хрупкий, его непосредственная адгезионная прочность невелика. Впоследствии нестехиометрический, пористый, игольчатый Cu₂S вырастает в резиновую матрицу, создавая механическое сцепление с вулканизатом. Предполагается, что двойные связи C=C в молекулах каучука могут образовывать ковалентные связи C–S с поверхностью Cu₂S. Таким образом, химическая связь и физическое сцепление являются двойным источником адгезии. Соли кобальта изменяют электрохимическое состояние поверхности раздела фаз, встраиваясь в решетку ZnO, тем самым подавляя избыточное образование ZnS, и способствуют росту Cu₂S. Резорциноформальдегидная смола мигрирует на поверхность раздела фаз в процессе вулканизации и образует градиентную сетку, которая выполняет функции физического закрепления, барьерной защиты и амортизацию нагрузки на шину.

Ключевые слова: стальной корд для шин, латунное покрытие, механизм адгезии, соль кобальта.

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Introduction

Steel radial tires are integral components of modern transport systems, and their characteristics directly affect the safety, fuel efficiency, and durability of vehicles. As shown in Fig. 1, the steel cords in the breaker and carcass bear the main load and provide resistance to impacts. Thus, the quality of the interfacial adhesion between the steel cords and the rubber matrix is a key factor determining the overall structural integrity and service life of the tire. At the same time, due to unfavorable operating conditions or technological failures during tire production, delamination may occur between the two layers of the belayer, which is closely related to insufficient adhesion of the rubber to the steel cords [1–3]. Therefore, it is necessary to conduct in-depth studies of the adhesion mechanisms of the steel cord with various rubber compositions [4–7].

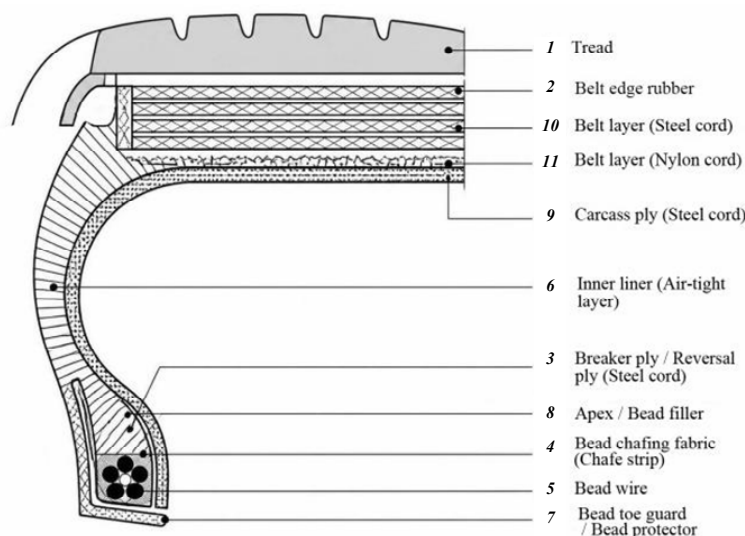


Fig. 1. Schematic diagram of the structure of an all-steel radial tire

The idea of the work is to examine the chemical composition of the surface of the brass coating of steel cord, the kinetics of the formation of the adhesive layer with the mechanism of dual adhesion [8], the mechanism of action of cobalt salts that stimulate adhesion [9], the interfacial functions of resorcinol-formaldehyde resin [10], as well as the mechanisms of aging and methods for controlling the adhesive layer [11]. The purpose of the review is to provide information that will help to better understand and optimize the characteristics of adhesive systems based on steel fiber and rubber.

Review methodology

This review is based on a systematic literature search of the Web of Science and Scopus databases using keywords including “rubber-brass adhesion,” “steel cord adhesion,” “cobalt adhesion promoter,” “resorcinol-formaldehyde resin,” and their combinations. The search timeframe spans 1978 to 2026, with emphasis on literature published after 2010 while also including earlier classic works. A total of 58 relevant publications were screened, covering original research, reviews, and conference papers. The inclusion criteria were: 1) direct relevance to the adhesion performance, interfacial characterization, or ageing behavior of rubber and brass-coated steel cords; and 2) provision of quantifiable adhesion strength data or explicit mechanistic analysis. Studies involving only fiber cords or non-brass coatings were excluded [12–14]. Based on the selected literature, this review organizes the discussion around three dimensions: interfacial chemistry, mechanisms of adhesion promoters, and ageing control [15–17].

1. Interfacial chemistry and physical mechanisms

1.1. Surface structure and initial state of brass coating

After vulcanization, the rubber compound can form strong adhesion with the brass coating, and the interfacial bond strength can even exceed the cohesive strength of the rubber itself [18]. The surface of the copper-plated steel cord naturally possesses an oxide film. During drawing and subsequent processing, zinc ions diffuse to the outermost layer, forming a composite structure dominated by ZnO with an extremely thin CuO layer superimposed. Van Ooij et al. confirmed through surface analysis that the thickness of the CuO layer is only about 0.5 nm. The structure and thickness of this oxide film have important effects on the formation of the adhesion layer during subsequent vulcanization: the ZnO layer serves both as a diffusion channel for Zn^{2+} and as a key target for cobalt salt action (Fig. 2).

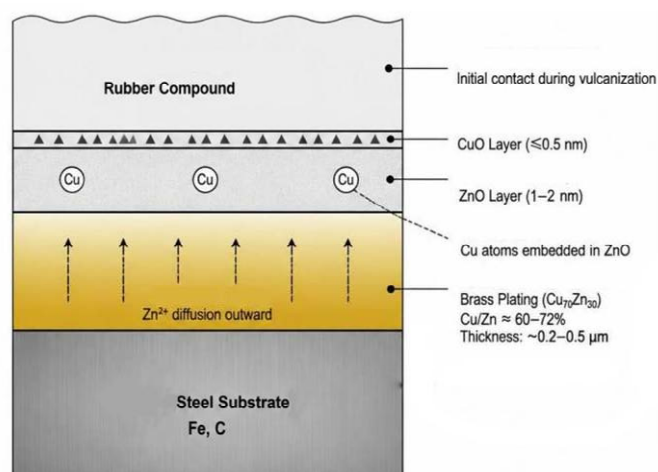


Fig. 2. Surface structure model of brass-coated steel cord

The phase composition and copper content of the brass coating are key factors affecting adhesion performance. Basheer et al. systematically reviewed the critical regulatory roles of brass phase composition, copper content, and coating thickness on rubber-brass adhesion. That review concluded that a Cu/Zn ratio in the range of 60 : 40–70 : 30 is a prerequisite for achieving optimal adhesion. When the copper content is too low, the amount of Cu_2S generated during vulcanization is insufficient to form effective mechanical interlocking; when the copper content is too high, excessive growth of the Cu_2S layer leads to increased brittleness and cohesive failure. Basheer et al. further pointed out that a coating thickness in the range of 0.15–0.30 μm provides the best balance between adhesion performance and processability. The crystal structure of the brass coating also affects adhesion performance.

1.2. Formation kinetics of adhesion layer: competitive growth of ZnS and Cu_2S

Tire vulcanization is typically carried out at about 150 °C in the presence of natural rubber surrounding the cord. The formation of the adhesion layer during vulcanization follows a strict thermodynamic and kinetic sequence. At the early stage of vulcanization, ZnS preferentially nucleates and grows on the brass surface. This occurs because the diffusion rate of Zn^{2+} in the ZnO layer is significantly higher than that of Cu^+ , and because the standard electrode potential of Zn^{2+}/Zn is lower than that of Cu^+/Cu , making Zn more readily oxidised and dissolved. HAXPES observations show that Cu_xS ($x \approx 2$) is detected in the adhesion layer at the initial stage of vulcanization, and Cu_xS is mainly enriched on the outermost surface of the adhesion layer. However, the ZnS layer is dense, brittle, and has extremely weak mechanical interlocking ability with rubber, contributing little direct adhesive strength.

1.3. Dual origin of adhesion: physical interlocking and chemical bonding

Classical adhesion theory holds that the mechanical interlocking formed by the porous needle-like Cu_2S layer growing into the rubber interior is the main source of adhesion [1]. However, recent surface analysis and theoretical calculations have confirmed the non-negligible contribution of chemical bonding (Fig. 3).

The synergistic effect of these multiple chemical interactions makes the binding energy of the rubber- Cu_2S interface significantly higher than that of simple physical adsorption. To maximise rubber-steel cord adhesion, three key conditions must be satisfied simultaneously: 1) the rubber compound has a high degree of unsaturation (e. g., natural rubber); 2) the sulfur content in the formulation exceeds 4 phr; and 3) the Cu/Zn mass ratio of the steel coating is in the range of 60 : 40–70 : 301,7.

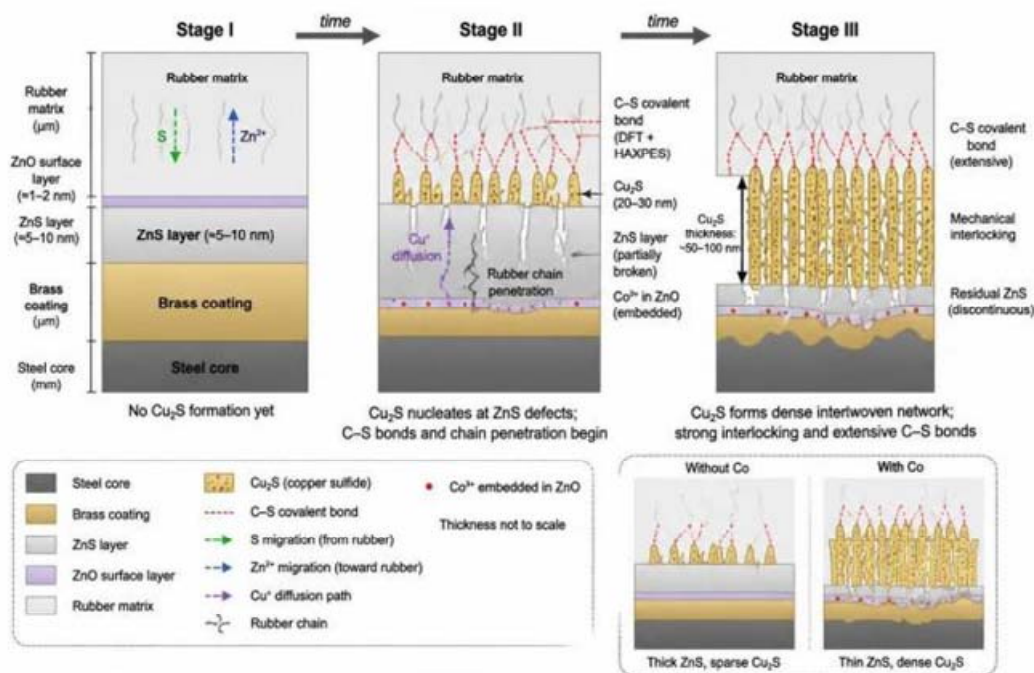


Fig. 3. Interfacial reaction model during vulcanization

2. Cobalt salt adhesion promoters

2.1. Types and industrial applications of cobalt salts

Cobalt salts have been used as adhesion promoters for rubber-brass-coated steel cords for several decades. The use of cobalt salts can achieve higher adhesion strength and rubber coverage on brass coatings, significantly improving adhesion performance. Rubber coverage is defined as the percentage of the steel cord surface area covered by rubber, as specified in ASTM D2229. Figure 4 shows a schematic comparison of the adhesion layer state before and after the addition of cobalt salt.

Numerous industrial cobalt salt varieties are available, including cobalt oleate, cobalt stearate, cobalt rosinate, and cobalt naphthenate. The main differences among cobalt salts lie in the type of organic acid group and cobalt content. In industrial practice, the appropriate cobalt salt type is usually selected on the basis of cobalt mass fraction and thermal stability, while also considering the effects of the organic acid group on compound processability and physical-mechanical properties [19].

The action of cobalt salts can also be understood from the perspective of vulcanization reaction kinetics. Studies by Chandra et al. have shown that cobalt salts can promote the generation of active sulfur species in the vulcanization system, increasing the sulfur

concentration available for Cu_2S formation at the interface [20]. At the same time, cobalt salts improve the initial wettability of rubber on the brass surface, facilitating interfacial contact and reaction uniformity at the early stage of vulcanization

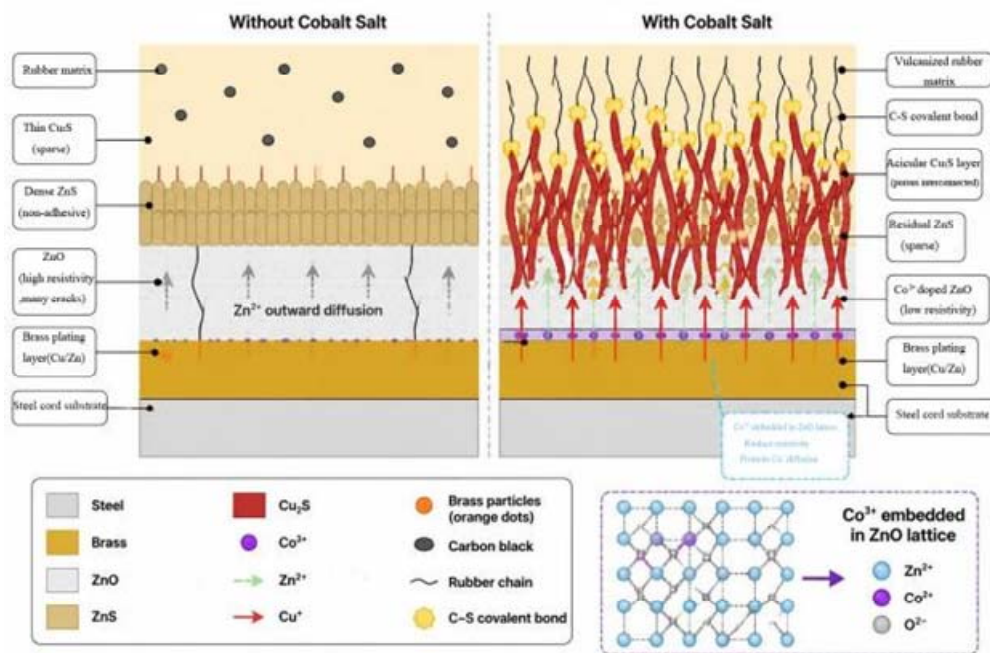


Fig. 4. Comparison of adhesion layer morphology with and without cobalt salt

From the perspective of electronic structure, theoretical calculations indicate that substitutional doping of cobalt ions (using Co^{3+} as a model) for Zn^{2+} in the ZnO lattice introduces additional electronic states, significantly reducing the bandgap of ZnO from 3.37 eV to about 2.8 eV. This change in electronic structure transforms the ZnO layer from an insulator to a semiconductor, significantly increasing the interfacial charge transfer rate. The increase in charge transfer rate directly shifts the electrochemical equilibrium of Zn^{2+} and Cu^+ at the interface in a direction favourable to Cu^+ migration, ultimately achieving optimised regulation of the ZnS/ Cu_2S growth ratio [17].

In summary, the roles of cobalt salts can be summarised as follows:

- incorporating into the ZnO lattice to reduce its resistivity and suppress ZnS formation;
- directly participating in the construction of the interfacial layer as Co_xS_y crystals, suppressing Cu/Zn diffusion and void formation [20];
- promoting vulcanization reactions at the interface and increasing the concentration of active sulfur available for Cu_2S formation;
- improving the initial wettability of rubber on the brass surface.

3. Resorcinol-formaldehyde resin interface mechanism

3.1. Interfacial migration and gradient distribution of resin network

At the early stage of vulcanization, owing to the polarity difference and surface energy gradient between the resorcinol-formaldehyde resin (polar) and the natural rubber matrix (essentially non-polar), resin molecules undergo thermodynamically driven spontaneous migration toward the compound-steel cord interface. This results in a resin-enriched gradient network layer on the brass coating surface, that is, on the outside of the Cu_2S adhesion layer.

Seo (1997) showed that the addition of RF resin significantly inhibits the migration of Cu and Zn from the brass coating to the rubber matrix during hydrothermal ageing [21]. AES depth profiling confirmed that in the unaged state, different RF resin contents show no significant differences in the interfacial adhesion layer, but during hydrothermal ageing, high RF resin content significantly suppresses the migration of copper and zinc to the rubber matrix. The mechanism is that the resin network forms a dense physical barrier layer at the interface, blocking the penetration and diffusion of water, oxygen, and corrosive ions. This conclusion has been further confirmed in subsequent studies. Furthermore, the stabilizing effect of the resin network on the adhesion layer can be summarized in two dimensions:

1) physical barrier function, in which the dense resin network layer blocks the penetration of water and oxygen to the interface, thereby inhibiting the dezincification ageing process of the brass coating;

2) mechanical buffering function, in which the modulus of the resin-enriched region, lying between the steel's approximately 200 GPa and the rubber matrix's few MPa, forms a gradient transition layer at the interface, effectively buffering the direct transmission of service stress to the brittle Cu_2S layer.

From the perspective of interfacial thermodynamics, the surface energy of RF resin lies between that of the brass coating and the natural rubber matrix. This surface energy gradient provides a thermodynamically favourable condition for spontaneous migration of resin to the interface. The resin that migrates to the interface can further enhance interfacial bonding through hydrogen bonds or coordination interactions between phenolic hydroxyl groups and the ZnO layer on the brass surface. During vulcanization, the resin network transforms from a linear prepolymer to a three-dimensional crosslinked structure via in situ crosslinking reactions, with crosslink density increasing by about one order of magnitude (Fig. 5). This change not only improves the mechanical strength of the resin network itself but also enhances its barrier efficiency against small molecules such as water and oxygen by reducing the free volume of the network.

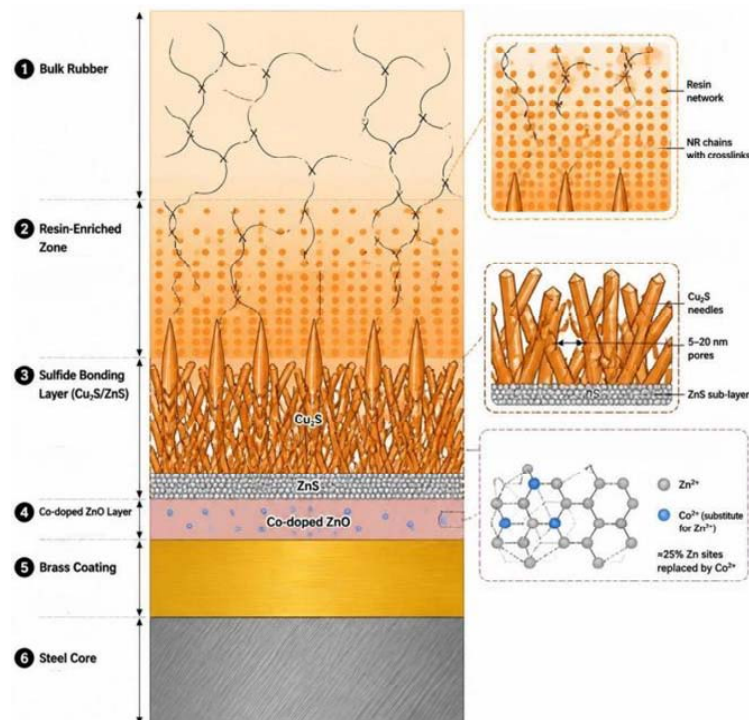


Fig. 5. Migration and gradient distribution of resorcinol-formaldehyde resin toward the interface during vulcanization

In summary, the functions of resorcinol-formaldehyde resin in rubber-brass adhesion can be summarised as three roles: 1) physical anchoring of the Cu_2S adhesion layer, complementary to the mechanical interlocking mechanism of Cu_2S itself; 2) physical barrier against corrosive media such as water and oxygen; and 3) mechanical buffering of interfacial stress.

Conclusions

Thus, the study of the adhesion mechanism between the brass coating and rubber has made it possible to establish that the physical adhesion of Cu_2S and the chemical bond C–S are two sources of adhesion. Covalent C–S bonds also contribute to adhesion, confirming that mechanical adhesion and chemical bonding together provide a dual source of adhesion force. Cobalt salts and resorcinol-formaldehyde resins play a key role in regulating interfacial interaction during vulcanization and in protecting the interfacial layer, respectively, forming a protection system. The adhesion is based on the physical bonding of the porous needle-like Cu_2S layer, which forms during the vulcanization process, with the rubber matrix, as well as the chemical bond C–S. Zinc sulfide is predominantly formed, but it does not directly participate in the adhesion. Traditional cobalt salts enhance adhesion due to a dual effect: they are incorporated into the crystal lattice of zinc oxide, changing the electrochemical state of the interfacial layer, and they directly participate in the formation of the interfacial layer in the form of Co_3S_2 crystals. Resorcinol formaldehyde resin forms a gradient network that performs three functions: physical anchoring, barrier protection, and mechanical buffering. During aging, the main cause of reduced adhesion under conditions of high humidity and temperature is desincercization. The combination of cobalt salt and resin significantly improves the retention of adhesion after aging.

The long-term service reliability of these new adhesion systems still requires further verification. Future development of adhesion systems will evolve toward high performance, long life, and green sustainability.

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