



## Adhesion of carbon steel and natural rubber by functionalized silane coupling agents



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### ARTICLE INFO

#### Keywords:

Silane coupling agent  
Carbon steel  
Natural rubber  
Functional groups  
Adhesion

### ABSTRACT

This study characterized a method of adhesion between uncured natural rubber and carbon steels (CS) by the surface modification of the CS with silane coupling agents comprising amino, thiol, glycidoxo, and isocyanate organic functionality. The effects of the functionalization of the silane coupling agents on adhesion between CS and uncured natural rubber were investigated by X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, atomic force microscopy, and local nanoscale thermal analysis. The reaction mechanism among the CS, silane coupling agent, and natural rubber was studied, revealing that adhesion was optimized and cohesive failure achieved when 3-(trimethoxysilyl)propylamine (APS) was used to modify the CS. The CS was shown to be directly silanized by the silane coupling agents, but the reactions between the natural rubber and the silane coupling agents was dependent on silane functionality.

### 1. Introduction

In recent years, adhesion technologies between rubber and metals have attracted much attention in the rubber industry. Rubber products such as tires, conveyor belts, and hydraulic tubes utilize the adhesion of rubber to brass-plated steel [1]. In modern tire technology, steel wires are bonded with rubber, forming a composite structure to enhance the structural support and mechanical stability of the tire [2]. Because unmodified steel has very poor adhesion to rubber, different coatings and various surface treatments for steel cords have been applied prior to tire manufacture to improve adhesion between the rubber and steel. Coatings of copper or copper-based binary or ternary alloys, such as bronze and brass, are the most commonly used materials to improve levels of adhesion between steel to rubber [3]. Copper-zinc brass coatings are used industrially for applications of steel tire cords in tire carcasses. At the interface between the Cu-based coated steel and the rubber, the formation of high-surface-area  $\text{Cu}_x\text{S}$  in the adhesion interphase is necessary for mechanical interlocking between the rubber and Cu-coated steel [4]. Although this plating process is very efficient, it is both expensive and environmentally unfavorable, as the brass electrodeposition process requires significant energy consumption during post-treatment thermal annealing. During the electrodeposition of the brass, many chemicals are used, and the treatment is not renewable [5].

Because of these limitations, the development of a lower-cost and less environmentally harmful process to promote adhesion between rubber and steel is of great interest. The replacement of the brass coating has been attempted by employing a polymeric adhesive interlayer, such as isoprene [6], thiophene [7], halogenated hydrocarbon [8], butadiene [9], nylon, and polyester [10], between the steel and rubber. In most studies, however, surface modifications using polymeric adhesives require plasma pretreatment or plasma-polymerized deposition, which increase the processing costs.

Silane coupling agents can provide hybrid linkages between organic matrices and inorganic reinforcements. They form thermodynamically stable covalent bonds with matrix polymers, as well as multiple inorganic bonds with favorable equilibrium constants for bond retention to the reinforcements [11]. This property has been applied to use silane coupling agents in providing or improving the adhesion strength between pairs of compounds such as metal and rubber [12], metal and resin [13], rubber and resin [14], glass and resin [15], and biomaterials [16]. Hergenrother et al. reported a method for improving and retaining metal adhesion to cured rubber through compositing an amino alkoxy-modified silsesquioxane with a rubber [17]. Coating the surface of the steel component with an organosilane compound was demonstrated to improve the hydrolytic stability of the adhesive bond between an organic adhesive and the steel [18]. Madeleine et al. reported an increase in the durability of joints between an epoxy

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powder coating and steel using the silane coupling agent  $\gamma$ -aminopropyltriethoxysilane [19]. However, the mechanisms of direct adhesion between steel and rubber using silane coupling agents have not been studied extensively.

Before entering the tire manufacturing line, some tire components are pre-formed, including the bead and steel belt components. Uncured rubber is typically pressed into and around steel cords as it is drawn through an extruding die. In this pre-forming process, the steel cords are insulated from each other and adhered to the uncured rubber [20]. In these components, the adhesion of the steel cord to the rubber must occur before the tire curing process. Additionally, the adhesion strength of steel cords with rubber does not correlate with compound crosslinking densities or other physical properties of the cured rubber [21]. Improving the understanding of the adhesion mechanism between steel cord and rubber has become necessary; an attempt to directly adhere rubber and steel cord without plating is the first step of this effort.

This study introduces a direct adhesion method between carbon steel (CS) and uncured natural rubber (NR) using four kinds of silane coupling agents functionalized with amino, thiol, glycidoxo, and isocyanate groups. The CS plates were modified by these different silane coupling agents and the surface characteristics of the treated CS plates were analyzed by X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), atomic force microscopy (AFM), and contact angle measurements. The adhesion strength between NR and CS when treated by the different silane coupling agents was measured by peel testing. Next, we investigated the reaction between different silane coupling agents and CS through local thermal analysis. Based on our investigations, we propose a mechanism for the excellent adhesion obtained with the use of silane coupling agents.

## 2. Experimental

### 2.1. Materials and reagents

CS (JIS S45C, VIPO A.S. Co.) was used as the tested metal. The NR (VIPO A.S. Co.) used in the study contained NR (100 phr), semi-reinforcing furnace (SRF) carbon black (50 phr), stearic acid (2 phr), ZnO as a stabilizer (5 phr), the curing accelerator N-cyclohexyl-2-benzothiazole sulfonamide (1 phr), and sulfur as curing agent (3 phr). The four kinds of silane coupling agents, 3-(aminopropyl)triethoxysilane (APS) (Shin-Etsu Chemical Co. Ltd.), (3-mercaptopropyl)trimethoxysilane (MPS), 3-glycidyloxypropyltrimethoxysilane (GPS), and 3-(triethoxysilyl)propyl isocyanate (IPS) were obtained at reagent grade (Wako Co. Ltd.) and used without further purification.

### 2.2. Surface treatment of carbon steel

The CS samples were treated by degreasing with acetone, immersing into a 10% v/v alcohol solution of one of the four kinds of silane coupling agents at room temperature for 1 s, and drying in air. The obtained CS samples were used for analysis and adhesion to NR. After surface modification by the different silane coupling agents, the analysis samples were kept in a vacuum for 24 h.

### 2.3. Adhesion process between CS and NR

Adhesion between the NR and CS surfaces treated by different silane coupling agents was accomplished by hot-pressing at 100 °C, below the curing temperature for NR, for 20 s under a pressure of 10 MPa.

### 2.4. Measurements

The CS blank and surface-treated samples were analyzed by XPS (PHI 5000 VersaProbe, ULVAC-PHI, Inc.) with a multi-technique

spectrometer, focusing monochromator (ULVAC-PHI, Inc.), and Al K $\alpha$  X-ray source with a 100- $\mu$ m-diameter spot for surface analysis. The pass energy of the analyzer was 23.5 eV for high-resolution scans at 25 W. The angle-resolved measurements were performed at an electron take-off angle of  $\theta = 45^\circ$ , where  $\theta$  is the angle between the sample surface and the direction of the analyzing photoelectrons. During the measurement process, an electron flood gun was used for charge neutralization and the analysis chamber was maintained at  $2.0 \times 10^{-6}$  Pa. The XPS spectra were subjected to the Shirley background subtraction formalism and the data was calibrated with the saturated C 1s peak at 284.8 eV, used to assign chemical bonding states. The full width at half maximum (FWHM) of the C-C/C-H component was permitted to vary freely; other components were fixed to accommodate the FWHM value. All XPS experimental curves were fitted to Gaussian-Lorentzian lines of variable proportion using MultiPak v.8.2 software (ULVAC-PHI, Inc.).

FTIR measurements were performed by a Thermo Nicolet Nexus 870 with the DuraScope attenuated total reflectance (ATR) accessory (Thermo Scientific Co.). Static contact angles were measured by an optical contact angle measuring instrument (G-1, Erma Inc.) with droplets of 1  $\mu$ L distilled water at 25 °C. The contact angle was measured at six different positions on each sample; the average of these values was reported as the contact angle.

The adhesion properties of the interfaces between the silane-bonded CS and NR were evaluated by peeling tests. The peeling test was performed using a tensile machine (IMADA Co., Ltd. mX-2500N), following the 90° type peeling test configuration at a crosshead speed of 50 mm/min at 25 °C.

The surface morphologies of the samples were measured by automatic AFM (Nanosurf EasyScan 2 AFM, Nanosurf AG Co.) in tapping mode. The images were recorded at a scanning rate of 0.7 s/line. Local thermal analyses were performed by combining a scanning probe microscope (Model SPM-9700, Shimadzu Co., Ltd.) and a nano-thermal analysis VESTA system (Model Nano-TA2, Anasys Instruments Corporation Co., Ltd.). The thermal probes (Model EX-AN2-300, Anasys Instruments Corporation Co., Ltd.) used for local thermal analysis had spring constants of  $\sim 0.1$ – $0.5$  N/m, tip radii < 30 nm, and upper limit temperatures of 400 °C. Measurements were taken at five points for every sample under a heating rate 10 °C/s.

## 3. Results and discussion

### 3.1. Surface chemical composition of CS surfaces treated by various silane coupling agents using XPS

The chemical compositions of the blank and treated CS surfaces were investigated by XPS. The high-resolution XPS spectra of the C1s and O1s orbitals of the CS surfaces after treatment by the four different silane coupling agents are shown in Fig. 1. The C1s spectra of the CS surfaces treated with different silane coupling agents have different shapes, as shown in Fig. 1(a). The untreated or blank CS surface shows a single peak of C-C/C-H. After treatment with silane coupling agents, the CS surfaces all show shoulder peaks at  $\sim 286.6$  eV, representing the C-O-Si bond [13]. However, the intensity of the C-O-Si peak from the APS-treated CS surface is lower than that from the surfaces treated by the other silane coupling agents. The hydroxysilane C-O-Si group in the silane coupling agent reacted with the steel to form a Metal-O-Si bond. On the surface of the IPS-treated CS, the peak for O=C=N at 288.5 eV [22] is observed, which is included in the IPS compound. From the O1s spectra of the differently treated CS surfaces, the blank CS shows a peak indicating FeO $_x$ , while the CS samples treated with APS, MPS, and IPS show methoxysilane or ethoxysilane groups. GPS-modified CS also shows a FeO $_x$  peak at 530 eV [23], implying that GPS does not completely cover the CS surface. These results showed that all four silane coupling agents reacted with or were absorbed on the CS surface.

To clarify the quantity of silane coupling agent on the CS surfaces,

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