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A new organofunctional methoxysilane bilayer system for promoting adhesion of epoxidized rubber to zinc
Part 1: Optimization of practical adhesion

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ABSTRACT

Practical adhesion of rubber to zinc cords is measured for various zinc silanization treatments. Aminopropyltrimethoxysilane (APS) alone or both APS and mercaptopropyltrimethoxysilane (γ-MPS) were used as coupling agents for zinc and epoxidized natural rubber (ENR). It is shown that special chemical and physical conditions are required to provide strong practical adhesion. With APS alone, best results are obtained when the zinc is silanized with 1% APS in isopropanol–water, cured at 110 °C for 1 h in air and vulcanized with ENR (20% epoxy groups) at 170 °C for 15 min. The adherence is further improved by double silanization with γ-MPS (0.5%) and then APS (1%). In both cases, the concentration of silanes, the cure temperature of the silane layers, the ageing and acidity of the silane solutions are the main parameters which must be thoroughly optimized. In the case of double silanization, the highest practical adhesion seems to be correlated with a true γ-MPS/APS bilayer structure which is achieved for a specific application of the γ-MPS. It is suggested that this layer is bound to zinc through its thiol function, and the APS layer (on the γ-MPS layer) is cross-linked to γ-MPS and ENR through silanol and epoxy groups, respectively. When the silanized zinc surface was vulcanized and the rubber then peeled off the zinc surface, XPS analysis of the bare zinc areas indicates a rupture characteristic of an adhesive failure in the case of silanization by APS alone, and a cohesive failure in the case of the double silanization.

1. Introduction

Since the 1960s, major improvements in tire quality have been achieved with the production of new radial-ply tires consisting of a composite structure of rubber and metallic wires, which is now standardized and produced by all manufacturers. This process has been extended to many other applications. However, the quality of the product depends greatly on the strength of the adhesion between the wire and the rubber. A well established technology has proved that with the use of a thin brass coating on steel cords, very good rubber–brass adhesion is achieved after vulcanization in the presence of sulfur compounds. The adhesion between natural rubber (NR) and brass, which is achieved during the cure process, results from the formation of an interfacial adhesive layer of zinc and copper sulfides. In Haemers' model [1] it is postulated that this adhesion is chemical and occurs through the penetration of NR-S_y groups (S_y are pendant sulfur groups attached to the natural rubber and resulting from the vulcanization step) into a sulfide film (Cu_xS with x ranging from 1.8 to 2), leading to Cu_xS-S_y-NR bonds. The Cu_xS layer is very thin and results from the diffusion towards the surface of Cu atoms through a ZnO layer and interact with S atoms released by rubber. The mechanism is complex and, thanks to the use of modern surface analysis techniques such as XPS, AES or SIMS, many refinements have been proposed to improve this model. Outstanding surveys can be found in several reviews [2], which establish an up-to-date model. In contrast to Haemers' model, it is assumed that mechanical adhesion is achieved through a tight interlocking of the polymer and the Cu_xS layer. It must be noted that the thickness and the porosity of the Cu_xS layer is critical. This process requires a careful control of vulcanization and rubber formulation with its corresponding ingredients (sulfur, nature of accelerator and value of its S to accelerator ratio, specific adhesion promoters and corrosion inhibitors) ([2c,d,e] and references therein). The multiplicity of ingredients and the control of their concentrations entail numerous technical difficulties. In particular, the use of cobalt salts and their additives as adhesion promoters, the need of a high S

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to accelerator ratio, both weaken the rubber mechanical properties and contribute to its over-heating [3,4]. Moreover, corrosion effects resulting from the steel–brass contact are also detrimental and not easily resolved.

For this a totally new strategy was proposed with the use of silane coupling agents instead of the previous technology based on copper coatings. Silane coupling agents [5,6], which have already been widely used in several surface applications, such as adhesion promoters for metals, polymeric and inorganic materials [7–11], appear to be good candidates. They allow to eliminate cobalt salts, to use various accelerators together with various sulfur to accelerator ratios, and as an additional advantage, they remain stable after prolonged overcure [12,13].

Obviously, this strategy requires that the organic alkoxysilane interacts with rubber and the metallic surface. The rubber must first be functionalized in order to bind with the silane and, secondly, the metallic surface must be oxidized to provide M-OH hydroxide groups available to condense with the SiOH groups. Thus, in practice, the metal is coated with an alkoxysilane solution of general formula X-R-Si$(OCH_3)_3$ (X being a functional group, i.e. NH_2, S_8, SH, etc., R being a spacer, in general a propyl group), and a condensation reaction occurs between M-OH and the –Si-OH groups of the hydrolysed alkoxysilane leading to M–O–Si–R–X after loss of H_2O. The group X is selected in order to interact with another group X′ grafted to the rubber (NR-X′), outstanding adhesion should be expected from the formation of covalent bonds (M–O–Si–R–X–X′–NR) between the two substrates.

First experiments following this technology and applied to rubber adhesives on aluminium were described by Thiedman et al. [14]. Application of this technology for improving the adhesion of brass and zinc tire cords to rubber was proposed later by van Ooij and co-workers [12] who used bifunctional polysulfide organosilanes and found significant improvements in adherence. It was assumed that double cross-linking occurred: a first bonding between the metal oxide and the hydrolysed silyl group, followed after heating by a second bonding between the silane sulfide groups and the rubber ethylenic bonds. At the same time, some of us [13] showed that adhesion could be dramatically improved by using epoxidized rubber and steel–zinc cords coated with aminoalkoxysilanes.

Although this adhesion mechanism which involves a coupling reaction between a metal and a functionalized polymer through the use of bifunctional alkoxysilanes is now well established and seems to be accepted, there are still several points which are not fully understood. In particular, it remains to be seen if the metal–silane interaction occurs only through the silanol functions. Adsorption of the other functional group of the silane on the metallic surface is *a priori* not excluded and this could modify the whole adherence between rubber and the metal. Moreover, it is worth examining how the M–O–Si– bonding behaves in an aggressive environment, in particular, in a moist environment. This is the reason why, in the case of zinc, we have considered a two-step procedure: a first reaction of a thiol-siloxane with the metal, for which exclusive formation of a strong Zn–S bond is expected, given that the affinity of thiol for zinc is high [15–19]. This zinc-modified surface is then reacted with a hydrolysed aminosiloxane, and the formation of an O–Si–O bridge is obtained by the condensation of the Si-OH groups of both silanes. Adhesion to ENR is then achieved through the formation of a covalent bond between epoxy and amino groups, and the result should be stronger adherence of epoxidized rubber to the zinc.

In this paper we describe results concerning the adhesion, the stability of the system in an aggressive environment, its optimization and a first characterization by X-ray photoelectron spectroscopy (XPS) of the silane bilayer. The detailed surface interactions of zinc with the silanes, the organization and the structure of the bilayer will be described by FTIR (Fourier transform infra-red spectroscopy), XPS and HREELS (high reflection electron energy loss spectroscopy) experiments in subsequent papers.

2. Experimental

In this study the steel wires were zinc-coated, the coupling agents were γ-mercaptopropyltrimethoxysilane HS-$(CH_2)_3$-Si$(O\text{-}CH_3)_3$ (γ-MPS), aminopropyltrimethoxysilane H_2N-$(CH_2)_3$-Si$(O\text{-}CH_3)_3$ (APS) and *N*-allylaminopropyl trimethoxysilane CH=CH-CH_2-NH-$(CH_2)_3$-Si$(O\text{-}CH_3)_3$ (NAAPS). In each case, the adherence of the metal to the ENR was measured under standard conditions by using a special mechanical set-up, providing the force required to extract the embedded zinc wire from the rubber (ASTM test N D2229/93).

2.1. Chemicals and sample preparation

APS and γ-MPS (both 97% pure), were obtained from Aldrich and used as received. NAAPS (95% pure) was obtained from ABCR (Karlsruhe, Germany) and also used as received. Silanes were dissolved in a mixture of ultra-pure water (Elga UHQ2; 18 MΩ cm) and isopropanol in the ratio 1/9 (v/v) and were used immediately (unless stated otherwise).

Rubber was provided by Bekaert and Continental. In standard conditions it contains 80% NR + 20% epoxidized natural rubber (ENR). This mixture is obtained by mixing 60% NR and 40% ENR-50 (NR epoxidized at 50%), this latter being added to react with the silane amino groups via epoxy groups. Additives are also present in this rubber mixture: carbon black N326 (60 phr), aromatic oils (5 phr), *N*-1,3-dimethylbutyl-*N*′-phenyl-*p*-phenylenediamine or 6PPD (2 phr), zinc oxide (5 phr), stearic acid (1 phr), *N*,*N*-dicyclohexylbenzothiazole-2-sulfeneamide (DCBS) (0.6 phr), and insoluble sulfur compounds (2.5 phr) (phr = parts per hundred rubber).

The steel cords provided by Bekaert consisted of seven steel wires twisted together (Fig. 1) and coated with a thin zinc layer (1–3 μm thick, 99.99% pure) deposited by electrolysis or by hot dipping.

2.2. Surface preparation

Several steps are required and must be optimized to obtain a zinc wire embedded in the epoxidized rubber with the best adherence.

The zinc surface must first be thoroughly cleaned. Among various chemical treatments available, we found that degreasing by ultrasonication in isopropanol (5 min), followed by treatment with HCl (0.01 M) for 1 min, and then by a modified RCA oxidizing process, was the most efficient (standard cleaning). A reproducible homogeneous oxidized zinc surface was obtained by treating the sample at 80 °C for 10 min with the $NH_3/H_2O_2/H_2O$ oxidizing mixture in the ratio 1/1/400 (v/v/v) (in the classical RCA treatment the proportions are 1/1/4, v/v).

Silanization of the zinc surface is the second step: in the case of the ‘single’ silanization the zinc sample is dip-coated into a freshly prepared (ageing time $t_{ag} = 0$) 1% APS water–isopropanol solution for 1 min at room temperature. The silanized-zinc wire is then dried under argon, hung in an oven and cured at 110 °C for about an hour in air. In a third step, the cured silanized sample is put in contact with epoxidized rubber (ENR), followed by vulcanization for 15 min at 170 °C.

In the case of ‘double’ silanization a first dip-coating adsorption is carried out with a 0.5% γ-MPS solution for 1 min at room temperature. As previously, the silanized layer is cured at $TC_1 = 110\,°C$