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Investigation of Organofunctional Phosphonic Acid Coupling Agents for Promoting Adhesion of Rubber to Zinc Plated Steel Cords

MASTER THESIS

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Assoc.Prof. Dipl.-Ing. Dr.techn. Gregor Trimmel

Institute for Chemistry and Technology of Materials

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AFFIDAVIT

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ABSTRACT

The practical adhesion of rubber to zinc is important for many technical applications where metal is used to reinforce the final rubber product. Zinc shows excellent corrosion resistance, which is important to ensure the reliability of many high performance products. This thesis investigates the use of organofunctional phosphonic acids as coupling agents to improve the rubber adhesion towards zinc plated steel wires. Phosphonic acids were chosen as adhesion promoters for their ability to form well packed self-assembled monolayers on various metal surfaces and their commercial availability. Together with an organofunctional group that is able to bind the rubber matrix during vulcanization, a strong chemical bond should be formed between the rubber and the metal.

In the first part the modification of the plated zinc surface with the phosphonic acid coupling agents was investigated. 10-Undecenylphosphonic acid, (3-aminopropyl)phosphonic acid and 12-mercaptododecylphosphonic acid were deposited onto the metal surface using different parameters in a simple dipping process. Then squalene, a liquid with a chemical structure similar to that of natural rubber, was used in the second part to predict the behavior of the coupling agent coated wires during the vulcanization process with real rubber systems. In the final part the treated wires were embedded inside of natural rubber, styrene butadiene rubber and ethylene propylene diene monomer rubber, vulcanized and finally, the pull-out forces were determined.

X-ray photoelectron spectroscopy and contact angle measurements showed that all three coupling agents successfully bound to the zinc oxide surface of the plated wires. Contact angle measurements also suggested that low concentrations of phosphonic acid in the precursor solution suffice for a successful coating with coupling agent. Pull out tests of the embedded wires were performed to compare the adhesive power of the differently treated substrates and the different rubber systems. Scanning electron microscopy and energy-dispersive X-ray spectroscopy were used to analyze the metal surface.

KURZFASSUNG

Die Haftung von Gummi auf Zink ist für viele technische Anwendungen wichtig, bei denen Metall verwendet wird um das finale Gummi-Produkt zu verstärken. Zink weist exzellente Korrosionsbeständigkeit auf, welche für die Langlebigkeit vieler Hochleistungsprodukte von großer Wichtigkeit ist. Diese Arbeit beschäftigt sich mit der Untersuchung von organofunktionellen Phosphonsäuren, welche als Haftvermittler die Haftung zwischen Gummi und zinkbeschichteten Stahldrähten verbessern sollen. Da Phosphonsäuren in der Lage sind dicht gepackte selbstorganisierte, monomolekulare Schichten auf verschiedenen Metalloberflächen auszubilden und aufgrund ihrer Handelsverfügbarkeit wurden sie als Haftvermittler ausgewählt. Zusammen mit der organofunktionellen Gruppe, der es möglich ist den Gummi während der Vulkanisation zu binden, soll eine starke, chemische Bindung zwischen dem Gummi und der Zinkoberfläche entstehen.

Im ersten Teil wurde die Modifizierung der Zinkoberfläche mit Phosphonsäure-Haftvermittlern untersucht. 10-Undecenylphosphonsäure, (3-Aminopropyl)phosphonsäure und 12-Mercaptododecylphosphonsäure wurden dafür mittels einer einfachen Tauchmethode unter variierenden Parametern auf die Metalloberfläche aufgebracht. Im zweiten Teil wurde Squalen, eine der chemischen Struktur von Naturkautschuk ähnelnden Flüssigkeit, verwendet um das Verhalten der beschichteten Drähte während der Vulkanisation mit echten Gummi Systemen abzuschätzen. Im letzten Teil wurden die Drähte in Naturkautschuk, Styrol-Butadien-Kautschuk und Ethylen-Propylen-Dien-Kautschuk eingebettet, vulkanisiert und anschließend wurden die Ausziehkräfte bestimmt.

Röntgenphotoelektronenspektroskopie und Kontaktwinkelmessungen zeigten, dass alle drei Haftvermittler erfolgreich auf die Oberfläche der Zink-beschichteten Drähte gebunden werden konnten. Kontaktwinkelmessungen zeigten auch, dass bereits eine kleine Konzentration der Phosphonsäure ausreicht, um die Drahtoberfläche mit diesen zu beschichten. Ausziehversuche der in Gummi eingebetteten Drähte wurden ausgeführt um die Stärke der Haftung der unterschiedlich modifizierten Drähte an die Gummisysteme zu vergleichen. Rasterelektronenmikroskopie und Energiedispersive Röntgenspektroskopie wurden letztlich verwendet um die Metalloberflächen zu analysieren.

ABBREVIATIONS

APPA	(3-Aminopropyl)phosphonic acid
CBS	N-cyclohexyl-2-benzothiazole sulfonamide
DCBS	N,N-Dicyclohexyl-2-benzothiazolsulfene amide
EDX	Energy-dispersive X-ray spectroscopy
EPDM	Ethylene propylene diene monomer rubber
MDPA	12-Mercaptododecylphosphonic acid
NR	Natural rubber
PA	Phosphonic acid
SBR	Styrene-butadiene rubber
SEM	Scanning electron microscopy
T-BAG	Tethering by aggregation and growth
UDPA	10-Undecenylphosphonic acid
XPS	X-ray photoelectron spectroscopy

TABLE OF CONTENTS

1 INTRODUCTION

Rubber is known for its versatile properties and is used in many technical products. This makes it a resource of high demand with annual consumption steady on the rise as seen in Figure 1. The applications are diverse but can be categorized into two main categories: tire-products and non-tire-products. 70 % of the natural rubber consumption can be attributed towards tire production[1]. Non-tire-applications include conveyor belts or v-belts, transport systems, handrails and hydraulic hoses. They all have in common that steel reinforcements are commonly implemented inside the rubber matrix to strengthen the final product, increase its stability and prolong its lifespan in general. The quality of those products is highly dependent on the strength of the rubber-metal bond which is why great efforts have been made to improve the adhesion towards each other [2][3].

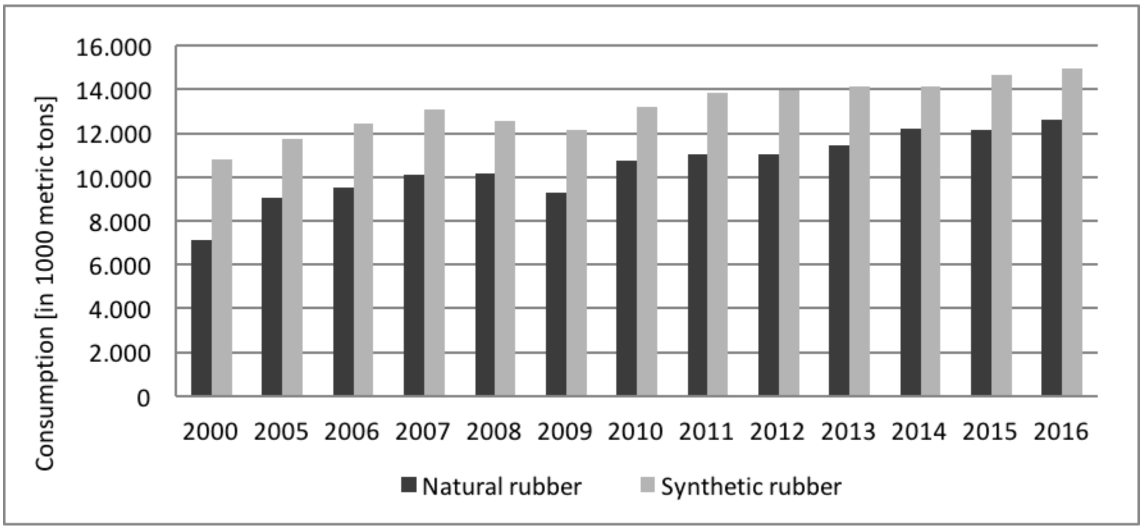


Figure 1. development of the annual consumption of natural and synthetic rubber from the years 2000-2016. (data taken from Statista)[3]

A well-established method to create strong rubber-metal adhesion consists of the implementation of brass coated steel cords inside the rubber product. In the presence of sulfur compounds brass is able to develop sulfide dendrites during the vulcanization process which physically interlock with the rubber matrix on top of it. Chemical interactions only play a minor role in this system. This process results in strong adhesion that hardly fails when performed correctly [2], [4].

However certain disadvantages and limitations of brass coatings make alternative coatings desirable for certain applications. Especially the low corrosion resistance of brass makes it unviable for some industrial applications. This is why zinc is often used when excellent corrosion resistance is required. But the adhesion mechanism where Cu_xS dendrites lead to a mechanical adhesion via interlocking does not apply to zinc coatings systems in the same way it does to brass coatings. Therefore the investigation and characterization of different bonding mechanisms is desirable to overcome this issue and to improve the adhesion of rubber to zinc. A promising approach consists of the establishment of a chemical bond between the rubber and the metal coating using coupling agents as adhesion promoters[2].

Phosphonic acids are known to be able to form self-assembled monolayers on various metal oxides and have shown great results in their ability to modify surfaces in previous studies [5]–[12]. Together with a functional group that is able to bind the rubber matrix during vulcanization, a strong chemical bond should be formed between the rubber and the metal. This alternative approach is investigated in this study by using organofunctional phosphonic acids to bind rubber to zinc coated steel wires.

2 THEORETICAL BACKGROUND

2.1 METAL-RUBBER ADHESION

2.1.1 RUBBER-ADHESION ON STEEL CORDS

Products, in which rubber is bound to metal surfaces are highly demanded and increasingly find use in various applications. In 98 % of the world's passenger tires, coated steel cords are embedded inside the rubber matrix to reinforce specific elements and areas in the rubber part. Rubber-metal adhesion is also important in non-tire applications like hydraulic hoses and handrails. This gives manufacturers a great opportunity to optimize physical parameters, and customize the properties of the product as needed [13], [14].

The performance of these products is largely dependent on the quality of rubber-metal-bonds that are formed during the vulcanization process. Great strength and durability are desired to provide high quality products. Uncoated steel cords possess a porous surface layer of iron oxide, which prevents the adhesion of rubber on the metal. Iron also is prone to corrosion, which is why a protective coating is usually applied to prevent product failures [15]. Brass is commonly used, since it adheres strongly to rubber and failures of those systems hardly ever occur. The main reason that usually leads to failure is the degradation of the rubber, rather than a failure of adhesion to the metal [4].

2.1.2 RUBBER ADHESION TO BRASS:

The excellent adhesive properties of rubber to brass have been known since 1862 where Sanderson submitted a British patent where brass acts as an intermediate to bind rubber to iron or steel [16], [17]. Initially, studies like those of Haemers [18], [19] suggested, that covalent bondings between the brass and the rubber via $Cu_xS\text{-}S_y$-NR bonds were the main reason for the rubber to stick to the metal. Although the exact binding mechanisms are still not fully understood, more recent studies seem to agree that strong mechanical interlocking of copper sulfides, that builds up on the metal surface during the vulcanization process is the main attributer for the adhesion, and that chemical interactions between the rubber and the metal play only a minor role[13], [20].

Brass with a copper content between 67 % and 72 % has shown a maximum adhesion force towards rubber. But lower copper content retains adhesion better after aging under humid conditions, which is why brass for coating usually contains a copper content around 63.5 % copper (slightly below the maximum) [18], [21]. As illustrated in Figure 2 the brass coating and drawing process of the wire causes zinc ions to diffuse towards the surface, where they oxidize to ZnO, which is overgrown by a very thin Cu_2O layer. The composition as well as the layer thicknesses may vary depending on the drawing conditions of the wire [20]

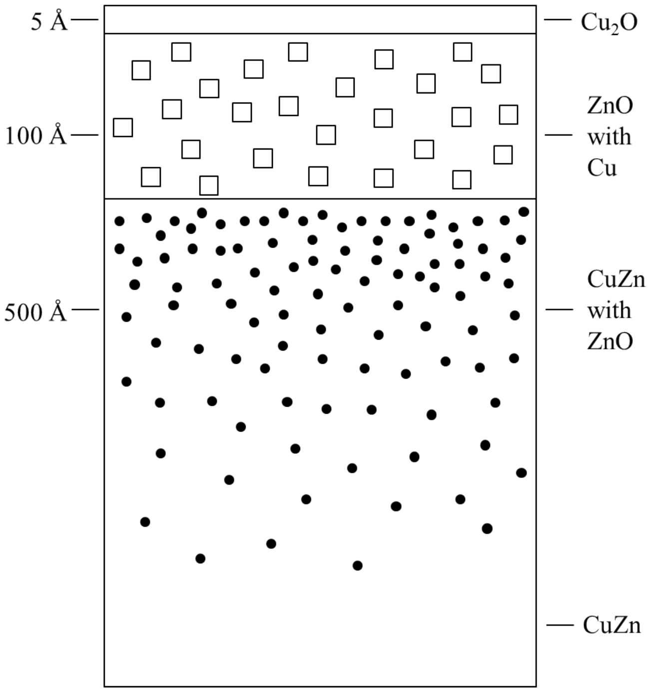


Figure 2. Diagram of brass-coated steel wire surface

Metal oxide structures contain various defects and imperfections, which allow diffusion processes to occur. At the start of the vulcanization, zinc ions, copper ions and free electrons diffuse to the surface via cationic diffusion. When they react with the active sulfur containing molecules in the rubber mixture, sulfides form via sulfidation. Zinc sulfides and copper sulfides have a tendency for phase segregation and they do not form simultaneously. Initially zinc sulfide is formed that gets overgrown by non-stoichiometric copper sulfide at a later stage of the vulcanization process. [22]

The initially formed ZnS layer hinders copper ions to diffuse through and makes zinc migrate faster towards the surface than copper due to the difference of their ionic radii[13], [23]. Once the copper ions pass the ZnS layer however, their diffusion rate increases significantly due to the non-stoichiometric nature of the overlaying Cu_xS layer. As seen in Figure 3., the copper ions form dendritic structures at the metal surface, which tightly interlock with the rubber matrix after it is crosslinked. This dendritic Cu_xS buildup continues until the copper in the intermediate ZnO layer is used up, and no further sulfidation of copper ions can occur. [20]

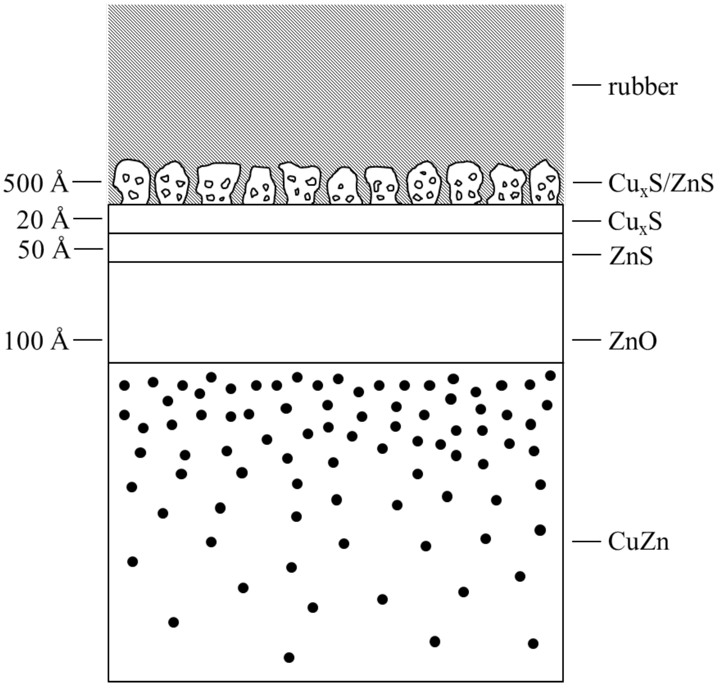


Figure 3. Diagram of a brass-rubber interface after the vulcanization. It shows the dendritic morphology and the mechanical interlocking with the rubber matrix.

If the initially formed ZnS layer was too thick, the migration of Cu-ions would be completely inhibited, which would furthermore prevent the formation of the dendritic Cu_xS structures, which are key to provide rubber-brass adhesion. On the other hand, if the initially formed ZnS layer would be too thin, Cu-ions could increasingly migrate to the surface. This excess of Cu-ions would consequently form large structures of Cu_xS which as a result would become brittle, break easily and finally would lead to a complete loss of adhesion properties [24]. The importance of the layer thickness further supports the theory of mechanical forces being the main contributors to the rubber brass adhesion rather than chemical interactions [4].

Even though rubber brass systems are mostly used today, there are disadvantages as well. A strong adhesion is only achieved when sulfur-vulcanization with a relatively high sulfur content (>4 phr) is performed [13]. The brass composition and their surface oxide layer are crucial for a good adhesion of rubber. Furthermore, only rubber systems with unsaturated bonds can be used, which limits the variety of rubbers able to adhere to the brass surface. Co-salts are essential to improve adhesion in the rubber-brass system, but they show negative effects towards the integrity of the polymer matrix. Also brass is not very corrosion resistant. The brass-rubber bonds are sensitive to corrosive environments and the direct electrical contact to the steel cord can cause accelerated corrosion when the brass is porous. This is also the reason why sometimes, when great corrosion resistance is required, zinc coated steel cords are used [22].

2.1.3 RUBBER-ADHESION TO ZINC

To counteract the disadvantages of brass coated steel cords, zinc coatings can be used as a coating for the steel cords. The most important commercial use of zinc is its application for protective coatings of carbon steel (galvanizing). It is commonly used in the constructive, automotive and due to the excellent corrosion protection of the underlying steel particularly the marine industry[25], [26]. In rubber products zinc is often used to reinforce conveyor belts, handlebars and hydraulic hoses to name a few. Zinc corrodes 5-100 times slower than steel in most natural environments [26], [27].This makes it an important coating for applications where exposure of the metal reinforced parts to the natural environment is possible.

Furthermore galvanic corrosion of zinc occurs when it is in contact with steel. Unlike with most other metals, it is a desired effect for this application in which zinc acts as a sacrificial coating to protect the integrity of the underlying steel. This effect zinc is mainly owing to its low position in the galvanic series [26], [28]. Apart from the better corrosion resistance, zinc coatings also show advantages in the processing. For example, it avoids the toxicity of the cyanide plating and the high heating costs of the diffusion plating during the brass coating process [29].

In principle, it should be possible for all metals that are able to react with the sulfurating species to form interlocking, dendritic sulfide structures. This should include the transition metal zinc. In reality however the sulfide growth with zinc is very slow and no sufficient dendritic sulfides are formed during the vulcanization process [22]. So, in order to achieve good adhesion between the zinc and rubber, another approach is usually applied. Despite the fact that zinc cannot form the excellent mechanical adhesion through the formation of an interlocking sulfide adhesion layer during vulcanization, zinc becomes a viable alternative for traditional brass coatings with the usage of adhesion promoters [2], [13], [29].

There are several adhesion promoter systems to choose from. A prominent one involves the surface pretreatment of the metal surface, where the surface gets covered with a coupling agent. This coupling agent can chemically or physically bind the rubber to the zinc surface. Among others, examples include silane, phosphonic acid and amine based coupling agents, which will be further discussed in the following chapters. They usually have an organic head group attached to it, which can interact with the polymer. Those head groups can vary depending on the used rubber system, which will be further explained in chapter 2.2.3 and 2.2.4.

Kang et al reported another system where they coated zinc plated steel cords with RF plasma polymers of butadiene or acetylene to improve the rubber adhesion[30]. The polymerization and the plasma etching were applied using argon plasma. Both systems enhanced the adhesion successfully. These samples showed pull-out forces around 285 N, which are similar to that of brass-plated steel filaments.

Adhesive resins are also commonly employed in rubber systems with metal or fiber reinforcements. The resins react with the metal and the rubber forming a reinforced bond between them. Conventionally a combination of hexamethylene-tetramine or hexamethoxymelanine and a phenol-formaldehyde condensation product is used. Often resorcinol is used for the latter, but it can be exchanged for resorcinol/formaldehyde condensation products to reduce fuming[13], [31]. They act as methylene donor and methylene acceptor and form a resin in-situ during the vulcanization of the rubber. Also resorcinol-free compositions were reported where the melanine derivatives are substituted, allowing self-condensing of the resin[32].

Further important adhesion promoters for rubber-zinc adhesion are metal coagents, which are the metallic salts of acrylic and methacrylic acids. In the presence of free radicals, they are very reactive and form highly crosslinked polymeric networks, which influence the physical properties of the cured rubber. In addition, they also increase the adhesion of rubber to metals during vulcanization. The coagents can simply be mixed with the entire rubber batch as an internal adhesion promoter for the compound. While this technique can be used for peroxide and sulfur cured systems, the metallic coagents do adversely influence the cure state of the sulfur compound [33].

Metallic coagents can also be used to form an adhesive strip with the rubber, which is then cured onto the metal. Then various rubber systems can be applied on top of that layer to be bound to the adhesive strip during the curing process. This way peroxide and sulfur vulcanized rubbers can be attached to the metal surface. Another technique involves a dispersion of the coagent, which is then applied onto the surface of the metal or the rubber stock. The rubber is then vulcanized on the metal forming adhesive bonds between them. However, this approach is limited to rubber containing peroxide as a curative to activate the reactive dispersion, like peroxide-cured EPDM rubber for example [33].

2.2 ADHESION PROMOTERS

Adhesion promoters or coupling agents act as an interface between an organic polymer and an inorganic material. It acts as a bridge or “glue” between the two materials, which are often very different in compatibility, reactivity or surface properties, to raise the adhesive forces between them. These chemical bonds between metal and rubber show high resistance against heat, irradiation, moisture and chemicals. This is why adhesion promoters also often create an additional barrier between the metal and the environment, acting as an additional protective coating for the metal. Those properties make coupling agent a viable option to improve the adhesion between the zinc coated steel cord and the rubber [34]

Adhesion promoters usually contain two functionalities on each end of their molecular structure. The first one is an anchor group to provide reactivity of the adhesion promoter towards the inorganic substrate. They enable chemisorption on various metals and metal oxides and will be further discussed in the chapters 2.2.1 and 2.2.2.

The second one consists of an organofunctional head group, which can react with the organic rubber and is connected by a spacer to the inorganic anchor group (see Figure 4). While adhesion promoters that are based on chemical bonds between the two materials are predominantly used, nonreactive adhesion promoters, using only Van der Waals or dipole interactions, also exist. Coupling agent head groups will be further discussed in chapter 2.2.3 and 2.2.4 [34]–[36].

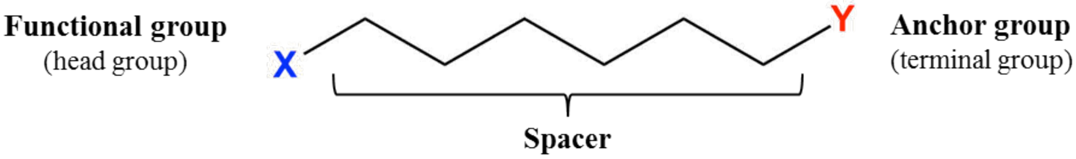


Figure 4. General structure of an organofunctional (bifunctional) molecule

In this thesis coupling agents are used to promote the adhesion of rubber to the surface of zinc plated steel cords. But adhesion promoters find use in various other applications as well. Those include mineral-filled composites, where mineral fillers require surface modification in reinforced plastic to improve the adhesion along the interface. They also include printed circuit board applications, where bonding of epoxy resin laminates to the glass surface is required. Furthermore, coupling agents are essential for the manufacture of encapsulating resins for solar cell modules. Similarly to metal reinforcements in rubber, fiberglass can be used as reinforcement in polymeric composites. Coupling agents act as adhesion promoters and as moisture protectors in those applications as well [34], [37], [38].

2.2.1 SILANE ADHESION PROMOTERS

Very common anchor groups for adhesion promoters are silanes, which are the predominant chemical type of coupling agent used. They are not solely used as coupling agents, but also find use in protective coatings or surface modifications to enhance corrosion resistance or polar properties of the coated metal surfaces or even combine both properties in one single application. They are versatile and can be deposited on a wide range of substrates [34]. The general structure is shown in Figure 5.

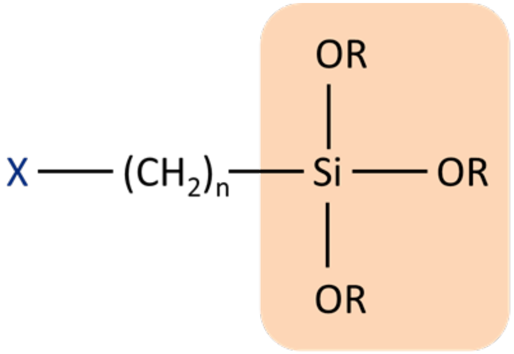


Figure 5. Principal structure of silane coupling agents. X corresponds to an organofunctional head group, which is able to interact with the polymer.

The nature of the Si-O-R groups enables robust chemical bonds, which are generally of stronger nature than physical bonds. Therefor they cannot be destroyed easily by heat, irradiation or moisture. The most common silane structures used for coupling agents are ones with hydrolysable alkoxy groups. In theory, a monolayer would suffice as a primer on the metal to obtain good adhesion with the rubber matrix to assemble. In practice however, multilayers, which form a condensed sol-gel network, act as the final bridge to connect the rubber to the metal in the final composite (see Figure 6).

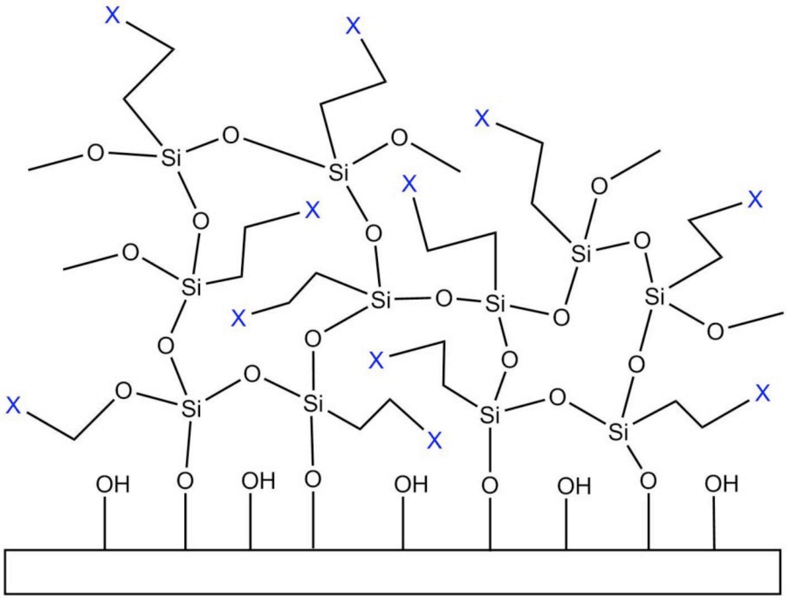


Figure 6. Sol-gel network of organofunctional silane coupling agents on the metal surface. X corresponds to an organofunctional head group that is able to interact with the polymer.

The generally accepted mechanism involves hydrolysis/condensation reactions between the silane coupling agents and the substrate as seen in Figure 7 [39]–[43]. The alkoxysilanes can be pre-hydrolyzed if the deposition is executed in water/alcohol mixtures. However, the hydrolysis can also occur slowly after the coating of the metal substrate took place with adsorbed water on the metal or from moisture in the environment. The non-hydrolysable organic terminal groups of the coupling agent ultimately react with the rubber matrix during the vulcanization process to ensure strong adhesion [34]–[36].

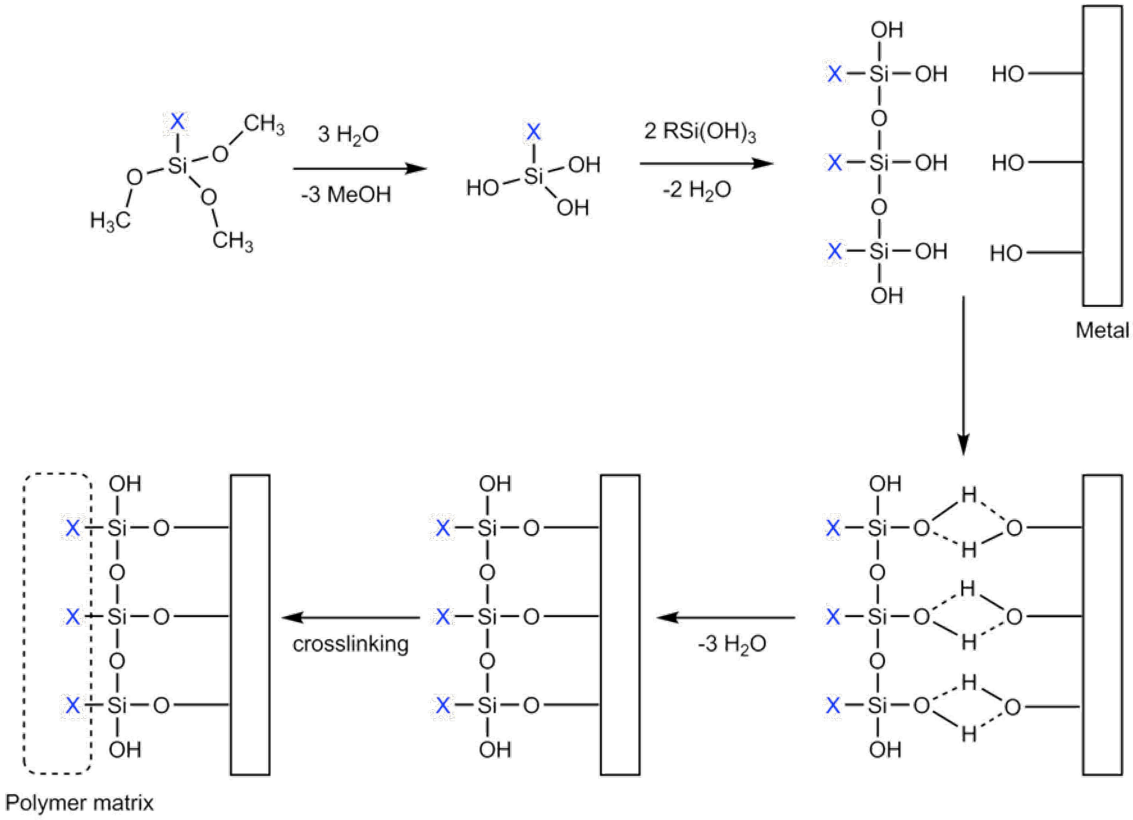


Figure 7. Hydrolysis, condensation reaction and further use of organosilanes. X corresponds to an organofunctional head group of the coupling agent.

It becomes clear that the nature of the metal oxide layer is important for the condensation reaction of the alkoxysilanes during the coating. The effectiveness of the bonding is strongly affected by the concentration of hydroxyl groups available on the metal surface. While aluminum, copper, tin and iron naturally exhibit good adhesion to organosilanes, zinc among other metals only poorly bind them [37]. This is why pretreatments, like plasma etching, are crucial to activate the surface of the zinc surface before coating with silane coupling agents can be performed [44], [45].

2.2.2 PHOSPHONIC ACID ADHESION PROMOTERS

Phosphonic acids (PAs) have been successfully used to tune the surfaces of metal oxides before. [5]–[8], [10]–[12], [46] Compared to silane coupling agents PAs are less sensitive to water, which spares certain deposition and storage constraints, which hydrolytically sensitive silane agent usually exhibit. Also, sol-gel networks are influenced by process parameters more severely than self-assembled, which negatively influences the reproducibility of silane coatings and requires higher effort to produce dry films. PAs however form well packed, homogeneous monolayers on the zinc oxide surface. The main reaction leading to the chemisorption of PAs again consists of a condensation reaction similarly to that of the alkoxysilanes shown in Figure 7. The three free binding sites of PAs allow for various binding modes on the metal surface that can be seen in Figure 8 [5], [6], [47], [48].

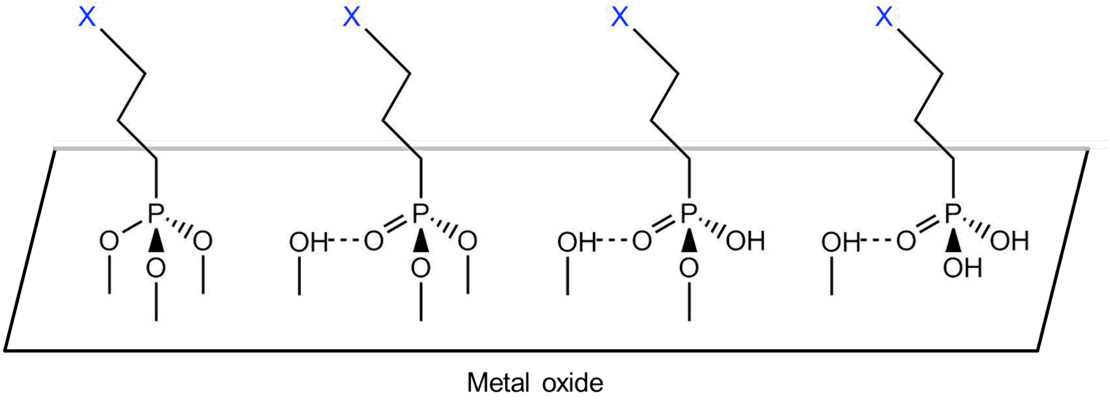


Figure 8. Some suggested bonding configurations of phosphonic acid coupling agents to metal oxides including tri-dentate, bi-dentate, mono-dentate and hydrogen bonds. X corresponds to an organofunctional head group [7].

A study by Hotchkiss et al. [5] concluded that phosphonic acids predominantly bind to ZnO surface in a tridentate fashion after a T-BAG deposition of the phosphonic acid on the substrate surface was performed, which further confirms strong binding properties by PA's that are required for a good adhesion interface. The T-BAG deposition was first described by Hanson et al [8] and is short for tethering by aggregation and growth. It is a straightforward process where the substrate is held vertically in a solution of phosphonic acid below its critical micelle concentration. Then the solvent is slowly evaporated leaving a monolayer of PA on the substrate surface that remains even after vigorous cleansing by sonification and is then heated to 140 °C to convert adsorbed PA to chemically bound PA. Another advantage of this monolayer setup is the well-defined orientation of the organic head groups towards the polymer matrix as seen in Figure 9 [49].

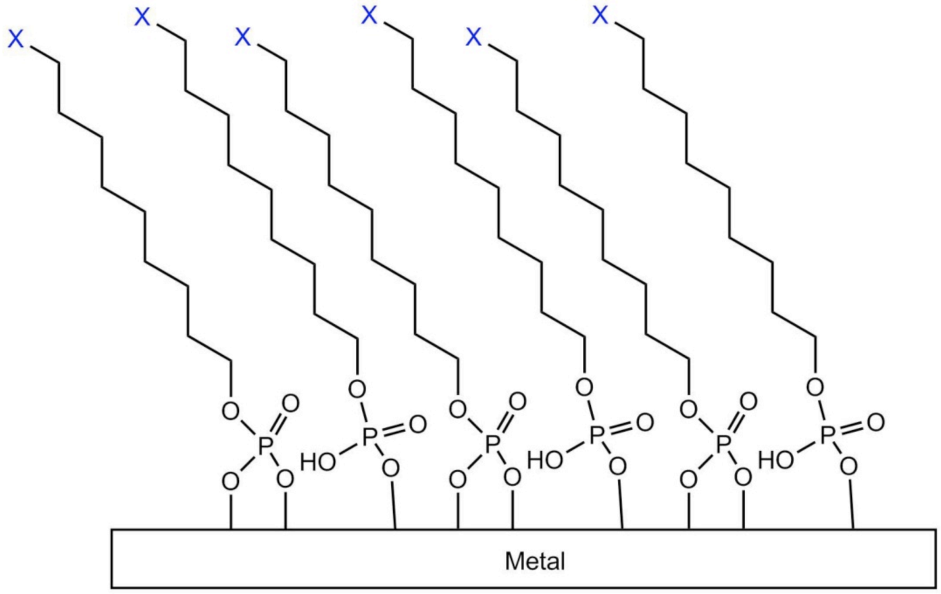


Figure 9. Proposed binding structure of long alkyl phosphate self-assembled monolayers [49].

Other alternatives to silanes include amine anchoring groups. But their inability to form robust monolayers is problematic [50], [51] and carboxylic acids, which tend to only weakly bind to the ZnO surface [52]. Organo-zirconates, zircoaluminates, chromates and organo-titanates have shown advances as adhesion promoters. The highly metallic nature of zircoaluminates enhances the reactivity with metal surfaces. Similarily organo-titanates are able to function as coupling agent via chemical adhesion to provide increased adhesion between the substrate and the rubber [34]. While thiols have shown promising results [53] a study of Perkins [54] has compared self-assembled monolayers on ZnO using thiol and phosphonic acid moieties with short alkyl groups attached. He concluded that PA-monolayers are preferred, due to their higher resistance against Brønsted acids, the formation of more uniform layers and a higher thermal stability compared to thiol monolayers. Phosphonic acids also show better chemical adsorption behavior to metal oxides compared to silanes [36], [55]. For those reasons phosphonic acid anchor groups are of great interest for the investigation of rubber to zinc plated steel cords.

2.2.3 ORGANIC HEAD GROUPS

The huge structural variability of organic molecules makes them attractive for functionalizing materials. Due to this, chemists can apply them seeking for specific properties. This variety also makes way for many different phosphonic acids to choose from as adhesion promoter. While data of phosphonic acid coupling agents for rubber adhesion on metal are rare, there are still many commercially available options to choose from. This flexibility regarding the organic head group makes it possible to choose the optimal functionality specifically for the rubber used in the desired composite. So, in theory it should be possible to integrate zinc coated steel cords in a variety of polymer systems.

When choosing a head group, a long spacer enhances the stability of the monolayers due to increased van der Waals forces between the alkyl chains forming a well packed crystalline like setup of the molecules. Also, a long alkyl chain allows for both functional groups to react independently from each other [36], [49]

The inorganic head group sticking out from the surface at the end of the spacer is also responsible for the change of wettability of the surface area. This modification of the surface can be used to create water repellant surfaces by choosing nonpolar functionalities for the head groups. It can also help to draw conclusions about the coverage of the substrate surface by the coupling agent using contact angle measurements. This can be helpful to conclude if the coating of phosphonic acid on the zinc surface was successful or not.

2.2.4 COMPATIBILITY WITH THE ORGANIC POLYMER

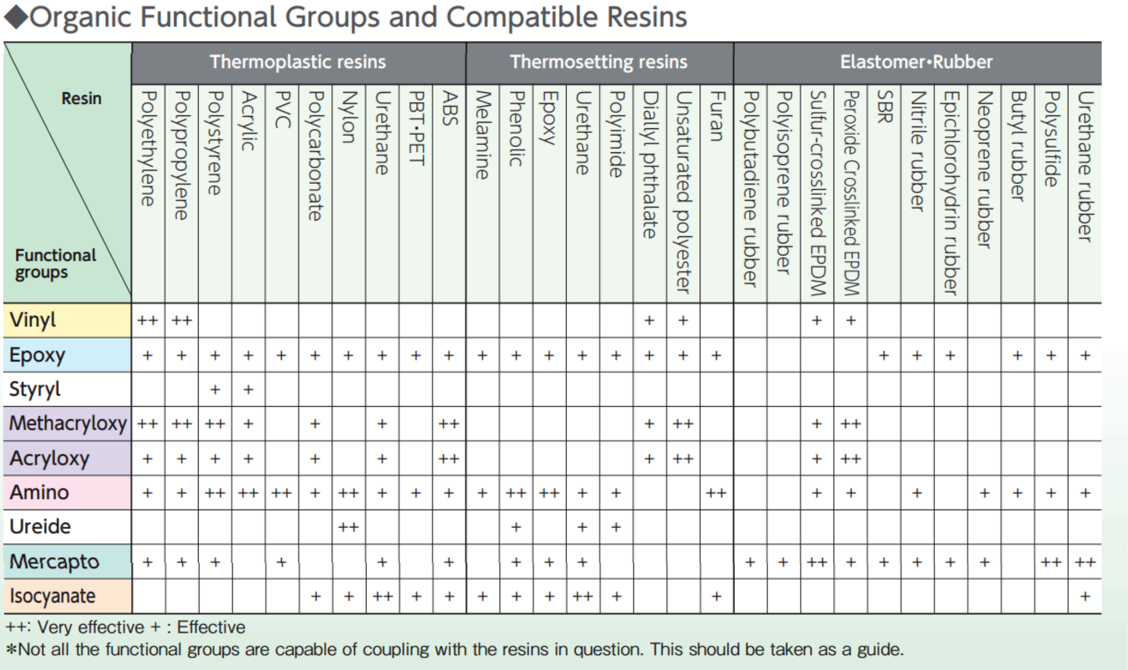
The most important thing for the organic head group is to be compatible with the polymer it is supposed to bind to the metal. This means, that it should be able to participate in the crosslinking process of the polymer, or be able to bind directly to the macromolecule. The interactions of the head group and the organic polymer are complex and diverse.

In thermoset polymers, it is optimal for the organofunctional group to participate in the curing process or for it to be able to attach to the polymer in some reactive way. For example, epoxy or amino groups can participate in the curing process of epoxy resins. Methacrylates can bind freely to unsaturated polyester resins during their curing through free radical crosslinking. Chloralkyl, epoxy or amino groups can also bind phenolic resins via several different reaction modes, making them viable head groups for those resins [34], [56].

For thermoplastic polymers like polypropylene and polyethylene the lack of reactivity to the polymer backbone makes covalent bonding of the coupling agent difficult. In these cases, interdiffusion of the coupling agent into the polymer matrix contributes strongly to the adhesion promotion. For example, when tripenylphosphine or cobalt acetylacetonate primers are applied and ethyl cyanoacrylate is used to form an adhesive bond to the polyolefin [57].Other examples include polyvinylchloride plastisols adhering to silane treated glass [58] and mercaptopropyltrimethoxysilane modified epoxy primers for crosslinkable ethylene-vinyl acetate copolymers in solar panels. [34], [59].

For elastromers/rubbers polysulfides are common coupling agents. They were investigated in studies by Jayaseelan and van Ooij in 2003 [29] and Mutin in 2009 [55]. They concluded that it is possible to achieve great adhesion on various metals including zinc. By integrating polysulfide chains from the active sulfur species in the rubber during sulfur vulcanization, the coupling agent can react with the allyl hydrogen atom of the unsaturated rubber. This means that covalent binding between rubber and the metal can be established. Bis-tetrasulfides are still commonly used as head groups for coupling agents in sulfur vulcanized systems.

Other important coupling head groups include amines which are known to be able to react with peroxide crosslinked EPDM. The amine function can participate in an epoxide ring opening reaction binding into the rubber structure [37], [38]. This is an example where no sulfur vulcanization is needed for the rubber system to adhere to the metal substrate. So despite the low compatibility with polyisoprene- and styrene-butadiene-rubber, amino functionalized adhesion promoters can react with peroxide crosslinked EPDM-rubber and epoxydized rubber, which makes them a viable option for many applications Another very popular head group is a thiol function commonly found in mercaptopropyltrimethoxysilane, which behaves similarly to the polysufide group and can react with a variety of systems [60]. For this reason mercapto functionalized PAs are of great interest, for their compatibility with polyisoprene-, styrene-butadiene- and EPDM-rubber promises a high potential to improve the adhesion of the rubber to the zinc plated substrate [38]. Figure 10 shows a chart of reactivity for various functional head groups and polymer systems.



◆Organic Functional Groups and Compatible Resins

Resin / Functional groups	Thermoplastic resins										Thermosetting resins								Elastomer·Rubber										
	Polyethylene	Polypropylene	Polystyrene	Acrylic	PVC	Polycarbonate	Nylon	Urethane	PBT·PET	ABS	Melamine	Phenolic	Epoxy	Urethane	Polyimide	Diallyl phthalate	Unsaturated polyester	Furan	Polybutadiene rubber	Polyisoprene rubber	Sulfur-crosslinked EPDM	Peroxide Crosslinked EPDM	SBR	Nitrile rubber	Epichlorohydrin rubber	Neoprene rubber	Butyl rubber	Polysulfide	Urethane rubber
Vinyl	++	++														+	+				+	+							
Epoxy	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+					+	+	+		+	+	+
Styryl			+	+																									
Methacryloxy	++	++	++	+		+		+		++						+	++				+	++							
Acryloxy	+	+	+	+		+		+		++						+	++				+	++							
Amino	+	+	++	++	++	+	++	+	+	+	+	++	++	+	+			++			+	+		+		+	+	+	+
Ureide							++					+		+	+														
Mercapto	+	+	+		+			+		+		+	+	+					+	+	++	+	+	+	+	+		++	++
Isocyanate						+	+	++	+	+	+	+	+	++	+			+											+

++: Very effective + : Effective

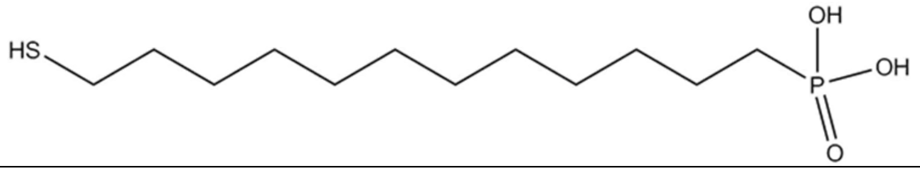
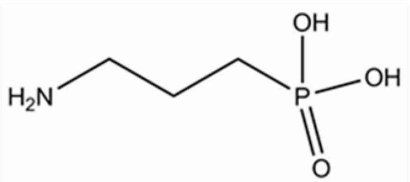
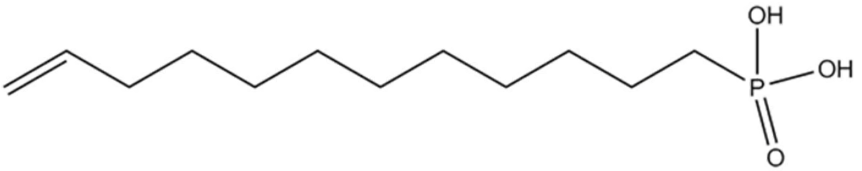
*Not all the functional groups are capable of coupling with the resins in question. This should be taken as a guide.

Figure 10. Chart of reactivity for various functional head groups and polymer systems. Taken from Shin Etsu [38]

3 AIM OF THIS THESIS

The aim of this thesis is to investigate the adhesion of rubber to zinc coated steel cords using bifunctional phosphonic acid coupling agents. Since the traditional mechanical adhesion mechanism of rubber to brass does not apply to zinc coated steel cords an alternative approach using chemical interactions was used. Phosphonic acids (PAs) were chosen as adhesion promoters for their ability to form well packed self-assembled monolayers on various metal surfaces and their commercial availability. The selection of adhesion promoters can be seen in Table 1.

Table 1. Selection of organofunctional phosphonic acid adhesion promoters.

12-Mercaptododecylphosphonic acid (MDPA) 
(3-Aminopropyl)phosphonic acid (APPA) 
10-Undecenylphosphonic acid (UDPA) 

The mercapto functionalized PA (MDPA) was chosen for its compatibilities with polyisoprene-, styrene-butadiene- and EPDM-rubber. They promise a high potential to improve the adhesion of the investigated rubber systems to the zinc plated substrate. Also, despite the low compatibility with polyisoprene- and styrene-butadiene-rubber, an amino functionalized PA (APPA) was used, which can react with peroxide crosslinked EPDM-rubber. Lastly, a PA with a nonpolar vinyl functional group (UDPA) was chosen mainly to investigate changes in the wettability of the surface after the coating, which provides information about the coupling agent coverage on the substrate surface.

The study is roughly divided into three parts.

The first part covers the investigation of the modification process of the zinc plated wired with the phosphonic acid coupling agents. In this part the chosen PAs from Table 1 were deposited onto the zinc surface testing different processing parameters. The determination of appropriate characterization methods is another important element in this section.

The second part discusses the investigation of the modified samples using a squalene mixture to mimic the conditions during the vulcanization process with rubber. The experiments are meant to estimate the behavior of the different coupling agents concerning the compatibility with rubber.

The third part consists of the investigation of the PA-coated wire substrates towards different rubber types. For this part NR, SBR and EPDM rubber were vulcanized onto modified zinc plated wires and pull out tests were performed. This was done to determine if the coupling agent was able to improve the adhesive strength of the rubber towards the metal.

4 EXPERIMENTAL

4.1 MATERIALS

4.1.1 SUBSTRATES

Table 2: List of the substrates used.

Substrate	**Source**	**Purity**
Zinc foil, 50x50x0.5 mm	Goodfellow	≥99.95 %
Zinc plated steel wires	Semperit Techn. Produkte GmbH	

4.1.2 CHEMICALS

Table 3: List of the used chemicals.

Chemical	**Source**	**Purity**
Tetrahydrofuran (THF)	Carl Roth	≥99.9 %
2-Propanol	Carl Roth	≥99.5 %
10-Undecenylphosphonic acid	abcr GmbH	
(3-Aminopropyl)phosphonic acid	abcr GmbH	
12-Mercaptododecylphosphonic acid	abcr GmbH	95 %
Vinylphosphonic acid	abcr GmbH	90 %
Diiodomethane	Sigma Aldrich	99 %
Squalene	Sigma Aldrich	technical
Zinc oxide	Semperit Techn. Produkte GmbH	technical
Stearic acid	Semperit Techn. Produkte GmbH	technical
N,N-Dicyclohexyl-2-benzothiazolsulfene amide (DCBS)	Semperit Techn. Produkte GmbH	technical
Cobalt stearate (Manobond CS 95),	Semperit Techn. Produkte GmbH	technical

9,3-9,8 % Co		
Naphtenic oil (Gravex)	Semperit Techn. Produkte GmbH	technical
Sulfur, oil content 5%	Semperit Techn. Produkte GmbH	technical
Ethylene propylene diene monomer (EPDM) rubber DUTRAL 4038	Semperit Techn. Produkte GmbH	technical
Natural rubber (CV 50)	Semperit Techn. Produkte GmbH	technical
Styrene-butadiene rubber KER 1500	Semperit Techn. Produkte GmbH	technical
Carbon black N 375	Semperit Techn. Produkte GmbH	technical
Carbon black N 550/SILO	Semperit Techn. Produkte GmbH	technical
N-cyclohexyl-2-benzothiazole sulfonamide (CBS)	Semperit Techn. Produkte GmbH	technical
Silica-kaolinite mixture SILLITIN N 85	Semperit Techn. Produkte GmbH	technical
Zinc salt DISPERGUM L	Semperit Techn. Produkte GmbH	technical
White oil	Semperit Techn. Produkte GmbH	technical
2,5-Dimethyl-2,5-di(tert-butylperoxy)hexane 45% silicone oil (Trigonox 101XL-45)	Semperit Techn. Produkte GmbH	technical

4.1.3 EQUIPMENT

Table 4. List of the used equipment.

Equipment	Source
O-plasma cleaner	FEMTO, Diener Electronic
Grinding and polishing machine	Struers LaboPol-25
Ultrasonic cleaner	VWR
Glovebox	M Braun MB 150B-G-II
Tube furnace systems	Nabertherm
Drop shape analysis system	DSA100 Krüss GmbH
Optical microscope	Olympus BX60
Camera	Olympus E-520
SEM/EDX	Quanta 600 scanning electron microscope
Vulcanisation press	KV141.1 Bucks Maschinenbau GmbH
Pull test machine	Zwick/Roell Z2.5
XPS	K-Alpha Thermo Fisher Scientific

4.2 COATING WITH SELF-ASSEMBLED MONOLAYER

The first step was to prepare the zinc plates and zinc plates steel wires by coating them with an adhesion promoter layer. The selection of adhesion promoters can be seen in Table 1.

4.2.1 PREPARATION OF THE PRECURSOR SOLUTIONS

The precursor solutions were prepared in 20 mL vials. 1 mmol/L of the PA coupling agent was dissolved in 5 mL THF for the experiments with zinc plates. Also, concentrations of 8.5 mmol/L, 1.0 mmol/L and 53.5 µmol/L UDPA were tested out, to investigate the influence of the precursor concentration on the final film.

For the experiments with the zinc coated steel wires 15 mL of 1 mmol/L coupling agent in THF were prepared in order to archive a higher level of solution in the vial to cover more of the wire’s surface. The vials were then closed and mixed properly before the substrates were immersed.

For the t-tests 60 wires had to be coated simultaneously for every coupling agent. In this case 140 mL stock solution with the concentration of 1 mmol/L coupling agent was prepared and distributed evenly among 6 glass test tubes.

4.2.2 SUBSTRATE PRETREATMENT

To guarantee that the metal surface on the zinc substrates is thoroughly covered with a monolayer of the coupling agent, and to improve the reproducibility of the measurements, some precautions had to be taken before the actual coating process.

Pretreatment of zinc-plates and zinc-coated steel cords

Round plates with the diameter of 1 cm were punched out of the zinc-foil. For the contact angle-, IR- -and the XPS-measurements, the plates were grinded since the roughness of the surface area has influence on the measurements. A clean substrate surface is key for successful coating, so the substrates were cleaned for 20 minutes in an ultrasonic bath with isopropanol, to remove residual dirt and oils from the surface. Immediately prior to the coating process, the substrates were plasma etched with O_2-plasma for 3 minutes to activate the surface and maximize the concentration of hydroxyl-groups, which is essential for the SAM to form (see Figure 7). To confirm the activation, contact angle measurements were performed before and after the plasma etching in a separate experiment. For the cords, the grinding step was skipped, and the cleaning and activation steps were carried out equivalently to those of the plates.

4.2.3 COATING OF SUBSTRATE WITH ADHESION PROMOTER

Immediately after the plasma etching, the clean, activated substrates were submersed in the precursor solution inside a vial, which was then sealed with a cap to prevent moisture from influencing the coating process. After 18 h the substrates were removed from the vial and rinsed with copious amounts of THF before further treatment was carried out.

For the t-tests 10 pretreated wires were immersed in every prepared test tube with the precursor solution. Then a plastic paraffin film was wrapped around the opening of the test tube. After 18 h the wire-substrates were removed and rinsed with THF before further treatment was performed.

4.2.4 FURTHER TREATMENT

To get rid of excessive coupling agent, the substrates were again cleaned for 10 minutes in an ultrasonic bath with isopropanol. Then the substrates were dried in a N_2-stream and temperature treated for 90 minutes at 150 °C on a heating element under N_2-atmosphere in a glovebox. The temperature treatment was tested at different conditions to investigate influences on the final film. Afterwards the substrates were stored under N_2 until further processing or measurements were performed.

4.3 SQUALENE EXPERIMENTS

For the squalene experiments, the following quantities shown in Table 5 were prepared.

Table 5. Quantities of substances used for the squalene experiments.

Substance	**Mass [g]**	**phr**
Squalene	50.0	100
Naphtenic oil	3.0	6
ZnO	3.5	7
Stearic acid	1.0	2
Co-stearate	0.5	1
DCBS	0.35	0.7
Sulfur	3.125	6.25

The squalene and the naphtenic oil were heated to 160 °C with an oil bath in a 50 mL round flask with a stirring bar. The mixture was stirred in a turbulent way to prevent an uneven exposure of the substrate to the squalene due to a steady flow direction. To achieve this, a cylindrical, non-ellipsoidal stirring bar was used in the round flask. Once the temperature was reached, the ZnO and the stearic acid were added and the mixture was stirred for 1 minute. Then the Co-stearate was added and the mixture was again stirred for 1 minute. DCBS and sulfur was then added and after another minute of stirring, the pretreated zinc coated wires, or the zinc-plates respectively, were immersed in the stirred mixture (see Figure 11).

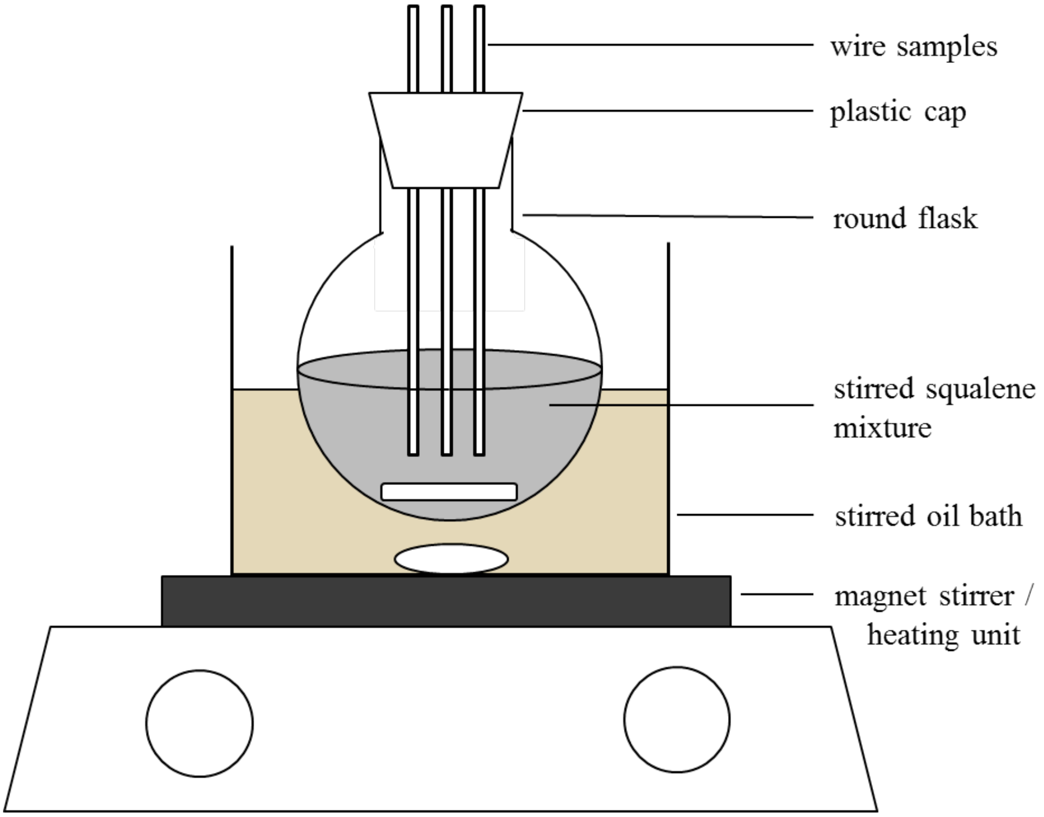


Figure 11. Sketch of the setup for the squalene experiments.

After 20 minutes the substrates were removed from the liquid and excess squalene-mixture was cleaned off the substrates surface by immersing it in toluene for a couple of seconds. Then they were dried and stored in a vial with N_2-atmosphere until further measurements were performed.

4.4 T-TESTS

The following NR and SBR mixtures were tested. The mixtures shown in Table 6 and Table 7 were prepared by *Semperit Techn. Produkte GmbH* in two sequential days. The sulfur and N-cyclohexyl-2-benzothiazole sulfonamide (CBS) were added on the second day.

Table 6. Quantities of the substances for the natural rubber mixture, which was used for the t-tests

Tradename	**Mass [kg]**	**phr**
CV 50 (NR)	0.7207	100
N375 ex RUSSIA.	0.5045	70
SOLV./PARAFF.	0.0649	9
ZNO ROTS.	0.0342	5
STEARIC ACID	0.0076	1
CBS*	0.0133	2
SULFUR 5%OIL	0.0216	3

Table 7 Quantities of the substances for the styrene-butadiene rubber mixture, which was used for the t-tests

Tradename	**Mass [kg]**	**phr**
KER 1500 (SBR)	0.7257	100
N375 ex RUSSIA.	0.5080	70
SOLV./PARAFF.	0.0653	9
ZNO ROTS.	0.0344	5
STEARIC ACID	0.0076	1
CBS*	0.0134	2
SULFUR 5%OIL	0.0218	3

In addition, an EPDM mixture with a peroxidic crosslinker was prepared by *Semperit Techn. Produkte GmbH* in one day. The quantities used for it are shown in Table 8 below

Table 8. Quantities of the substances for the ethylene propylene diene monomer rubber mixture, which was used for the t-tests

Tradename	Mass [kg]	phr
DUTRAL 4038 (EPDM)	0.6186	100
RUSS N 550/SILO	0.4176	68
SILLITIN N85	0.1268	20
DISPERGUM L	0.0062	1
WHITE OIL	0.1856	30
TRIGO.101XL-45	0.0402	6

Immediately before the vulcanization the rubber mixtures were rolled out to a thickness of 7.5 mm. The zinc coated steel cords, equipped with a layer of adhesion promoter, were placed between two stripes of rubber and the vulcanization was carried out in a vulcanization press at 160 °C and 320 bar for 20 minutes. 15 wires were processed simultaneously in one device with an embedment length of 10 mm per wire. After the vulcanization process was finished after 20 minutes, the wires with the rubber attached to them were removed from the pressing device and left for approximately 18 h before characterization of the adhesion strength was performed via pull out tests.

4.5 CHARACTERIZATIONS

4.5.1 CONTACT ANGLE MEASUREMENTS

The contact angle as well as the surface energy were measured using the Drop Shape Analysis System DSA100 (Krüss GmbH, Hamburg, Germany), a T1E CCD camera and the DSA1 v 1.90 software. The samples were measured on the same day the coating was finalized, in order to prevent eventual aging of the adhesion promoter layers from influencing the measurements. For the investigation 1.5 µL droplets of H_2O and diiodomethane were used in the sessile drop modus. The surface energy was calculated using the Owens-Wendt method. At least two different substrates were analyzed for each sample.

4.5.2 X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

The Zn-plates, which were coated with phosphonic acid adhesion promoters in advance, were investigated using an X-ray photoelectron spectroscope from Thermo Fisher Scientific. The source gun type was an Al K Alpha gun with a spot size of 400 µm in standard lens mode. The analyzer mode was CAE: pass energy 200.0 eV with an energy step size of 1.000 eV. The Thermo Avantage software was used to analyze the data. The surfaces of the zinc plated wire samples were measured after the coating with phosphonic acid coupling agents was performed. Another measurement was done after the wires were pulled out of the vulcanized rubber mixtures in the t-tests.

4.5.3 INFRARED REFLECTION-ABSORPTION SPECTROSCOPY (IRRAS)

The measurements were performed with a FT-IR spectrometer and a grazing angle accessory at 80 ° with a resolution of 4 cm^{-1} and an aperture size of 3 mm. To fit the apparatus zinc plates with the diameter of 2 mm were punched out, polished and then modified with the corresponding phosphonic acid coupling agent. 1000 scans were collected for each substrate. The spectra were analyzed in the Opus software.

4.5.4 PULL-OUT TESTS

The pull-out tests were performed on a Zwick/Roell Z2.5 testing machine. The wires were pulled out of the rubber at the rate of 100 mm/min with no preload being applied to them. The exposed wire was then characterized based on the amount of rubber still covering its surface from 0 to 3 (0 = 0 %, 1 = 1-49 %, 2 = 50 – 99%, 3 = 100 %).

4.5.5 SCANNING ELECTRON MICROSCOPY AND ENERGY-DISPERSIVE X-RAY SPECTROSCOPY (SEM-EDX)

The surfaces of the zinc plates were investigated with a Quanta 600 scanning electron microscope (SEM) that were coupled with an energy dispersive X-ray spectrometer (EDX) after squalene experiments were performed. The measurements were carried out under low vacuum and secondary and backscattered electrons were detected using LFD and SSD detectors. The atom% of the measured elements were normalized to Zn, because the Zn content does not change during the processing of the samples. Additionally, the surfaces of the wire-samples were investigated before and after the t-tests took place, to see if notable changes occur during the vulcanization.

5 RESULTS

5.1 PRETREATMENT AND COATING

The pretreatment of the metal and the parameters of the coupling agent coating process are of great importance to provide well packed self-assembled monolayers. To ensure a successful coating the metal surface needs to be as clean and smooth as possible. Furthermore, a high concentration of hydroxyl functions on the metal surface promotes the condensation reaction in which phosphonic acids mainly adsorb to the surface. It is also important to know the influence of the concentration of the precursor solution during the dipping process, as well as the influence of the temperature program after the coating was performed.

5.1.1 INFLUENCE OF THE PLASMA ETCHING ON THE ZINC SUBSTRATE SURFACE

Contact angle measurements were performed before and after the zinc plates were plasma etched. In both cases the zinc plates underwent a cleaning step in the ultrasonic bath but only one was plasma etched afterwards. The results are shown in Figure 12 and Table 9.

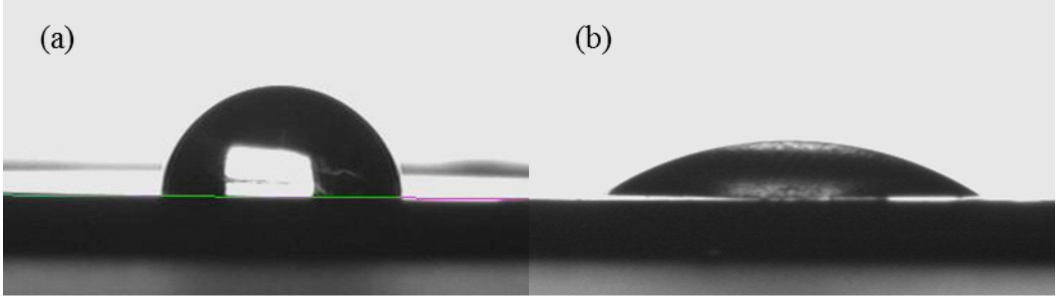


Figure 12. Comparison of the contact angles with water on (a) an untreated zinc plate, and (b) a plasma etched zinc plate.

Table 9. Contact angles and surface energies of zinc plates with plasma treatment and without plasma treatment.

Sample	H_2O [°]	I_2CH_2 [°]	Surface energy [mJ/m^2]
without plasma	81.4 ± 0.7	44.3 ± 2.4	40.9 ± 0.8
with plasma	29.2 ± 1.0	32.5 ± 3.4	70.8 ± 1.1

After plasma etching, the contact angle and surface energy of the substrates change considerably. As shown in Figure 12 the contact angle with water is lowered after the plasma treatment due to the higher polarity of the surface. Besides cleaning the surface from organic contaminations, the plasma treatment is also responsible for activating the surface by forming a controlled oxide layer consisting mostly of free OH-functionalities. This is desirable for the chemisorption of phosphonic acid coupling agents, which mainly consists of condensation reactions with free hydroxyl groups making plasma etching an important step in the coating process.

5.1.2 INFLUENCE OF PRECURSOR CONCENTRATION

UDPA was chosen to investigate concentration influences of the precursor solution. The standard preparation with zinc plates was performed, including the pretreatment and the temperature program at 150 °C for 1.5 h in the glovebox after the coating process. The resulting contact angle measurements of the coated substrates are shown in Table 10 and Figure 13.

Table 10. Contact angles and surface energies of UDPA coated zinc plates obtained with different precursor concentrations.

Precursor conc.	H_2O [°]	I_2CH_2 [°]	Surface energy [mJ/m^2]
8.5 mmol/L	114.9 ± 0.5	60.9 ± 5.2	27.9 ± 2.6
1.2 mmol/L	114.2 ± 0.5	63.9 ± 1.4	26.4 ± 0.3
53.5 µmol/L	110.9 ± 1.3	65.9 ± 2.4	25.2 ± 1.4
blank	44.5 ± 4.4	26.0 ± 3.0	64.4 ± 4.3

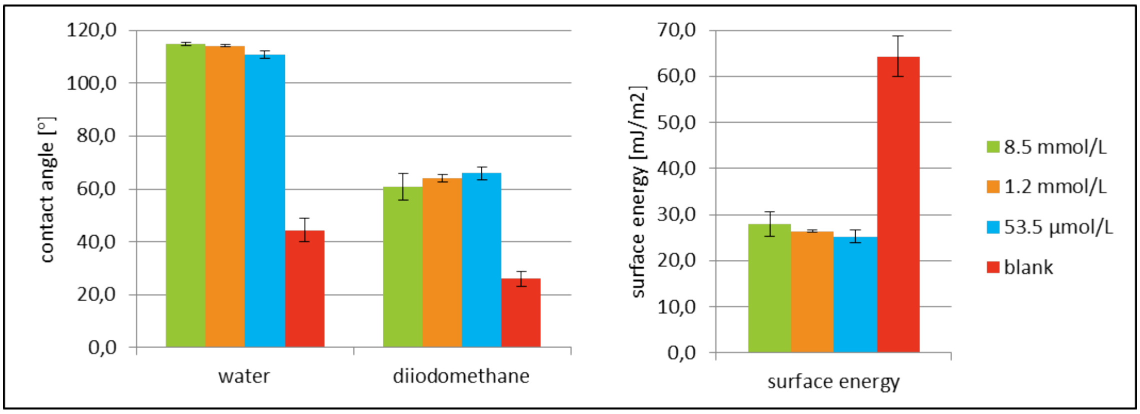


Figure 13. Comparison of the contact angles and surface energies of UDPA coated zinc plates obtained with different precursor concentrations.

The measured contact angles vary slightly between the different precursor solutions. This results in a modest decrease of the measured surface energy with decreasing precursor concentration. The presence of the precursor layer becomes evident when compared to a blank, which underwent the same processing steps. Generally, a very small amount of coupling agent is needed to coat the surface of the substrate with a monomolecular layer and the data suggests the influence of the precursor solution to be rather small. The results of the experiments demonstrate that even the concentration of 53.5 µmol/L coupling agent suffices for a successful formation of a SAM.

5.2 COATING WITH COUPLING AGENTS

5.2.1 INFLUENCE OF THE THERMAL TREATMENT

To promote the completion of chemical bonding thermal annealing at 150 °C for 90 minutes was performed. Hydrogen bonded PA-molecules are supposed to transform to covalently bonded phosphonates during this step. To investigate the influences of the coverage during the thermal treatment, UDPA coated substrate plates were tested under several conditions during the temperature step. The contact angle measurements of the resulting substrates are shown in Table 11.

Table 11. Contact angles and surface energies of UDPA coated zinc plates obtained with different heating conditions.

sample	conditions	H_2O [°]	I_2CH_2 [°]	Surface energy [mJ/m^2]
HP_Air	Heating plate / air	64.5 ± 0.1	36.9 ± 0.2	50.7 ± 0.1
HP_N_2	Heating plate / N_2	110.9 ± 1.2	65.9 ± 2.4	25.2 ± 1.4
O_Air	Oven / air	90.8 ± 9.9	45.9 ± 0.1	38.1 ± 1.6
O_N_2	Oven / N_2	104.6 ± 0.3	50.9 ± 2.9	32.6 ± 1.0
No_T	No temperature	113.0 ± 6.7	64.6 ± 0.3	26.1 ± 1.4

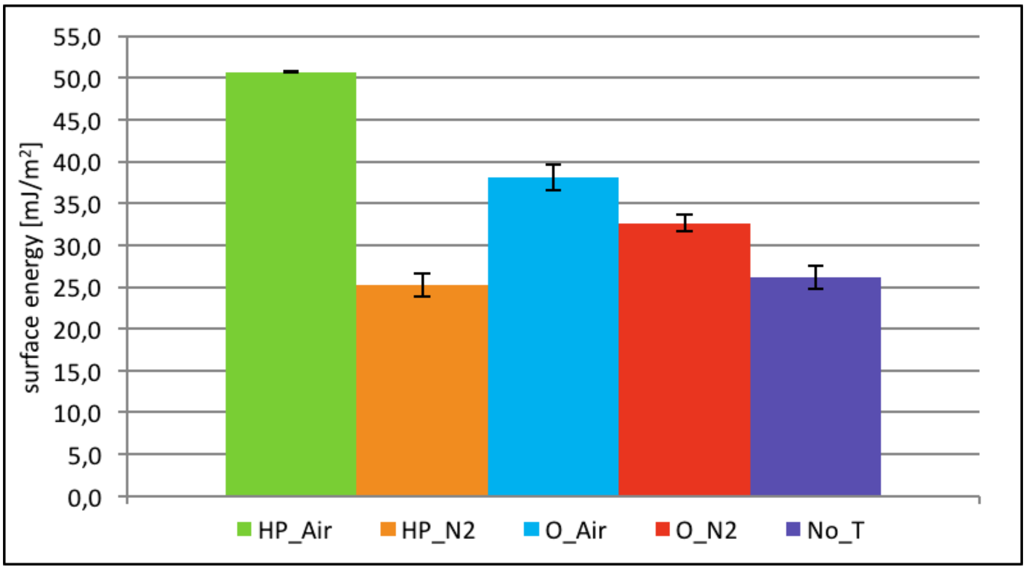


Figure 14. Comparison of the contact angles and surface energies of UDPA coated zinc plates obtained with different heating conditions.

When compared to the uncoated zinc blanks from Table 10 it becomes evident, that each temperature treated sample is still covered with a UDPA layer, causing the relatively low surface energy. Yet, while no SAM layer gets completely destroyed, differences depending on the temperature treating conditions become clear. Given that the No_T sample was well covered after the coating process, the increase in surface energy after the samples were treated under air indicates, that the coverage with UDPA compounds suffered. One possibility for the differences in the surface energies could be the results of oxidation processes that occur under ambient conditions that would raise the polarity of the surface. It is yet unclear if changes resulted from the metal oxide or the PA-layer, but it is advisable to perform the temperature annealing under inert atmosphere to prevent unwanted side reactions.

While all samples prepared under inert gas were able to maintain even lower surface energies, the substrates on the heating element were superior to those tempered in the oven. The high hydrophobicity correlates well with the expected results also shown by the similar octadecylphosphonic acid on zinc oxide substrates [5]. For this reason the temperature treatment under N_2 atmosphere on a heating element appears to be the preferred method for tempering the substrates.

Contact angle measurements only provide information about the coverage of coupling agent on the surface, but none about the binding state of the anchor group to the substrate. For further information regarding the binding modes XPS and IRRAS measurements can give insight to the layer quality after temperature treatment.

5.2.2 INFLUENCE OF THE ADHESION PROMOTERS

Comparison of contact angle

The surfaces of zinc substrates, which were modified by three different coupling agents, were investigated by performing contact angle measurements after the temperature treatment. The results can be seen in Table 12 and Figure 15

Table 12. Contact angles and surface energies of coated zinc plates obtained with different PA-coupling agents

Coupling agent	H_2O [°]	I_2CH_2 [°]	Surface energy [mJ/m^2]
UDPA (10-Undecenyl-PA)	117.9 ± 1.1	73.9 ± 1.8	20.8 ± 1.0
MDPA (12-Mercaptododecyl-PA)	90.7 ± 7.6	27.3 ± 2.2	46.0 ± 0.1
APPA (3-Aminopropyl-PA)	55.2 ± 1.5	40.2 ± 0.9	54.8 ± 0.6
blank	40.9 ± 3.0	38.4 ± 2.1	63.4 ± 1.2

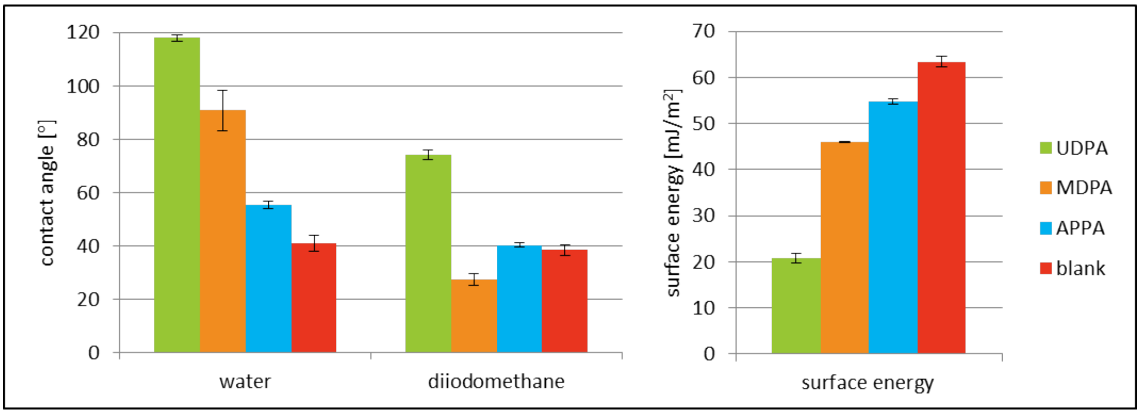


Figure 15. Comparison of the contact angles and surface energies of coated zinc plates obtained with different PA-coupling agents.

As expected, the contact angles and surface energies vary between the different coupling agents. The variation correlates with the polarity of the head groups of the different coupling agents. The ranked polarity (from polar to nonpolar) of the functional groups is amine>thiol>alkene. Respectively the surface energy falls in the same order with APPA>MDPA>UDPA. This makes the presence of the correlating phosphonic acids on the surface evident.

XPS-Analysis

To further confirm the presence of the phosphonic acid coupling agents XPS-measurements were performed. The results of the P(2p)-scans can be seen in Figure 16

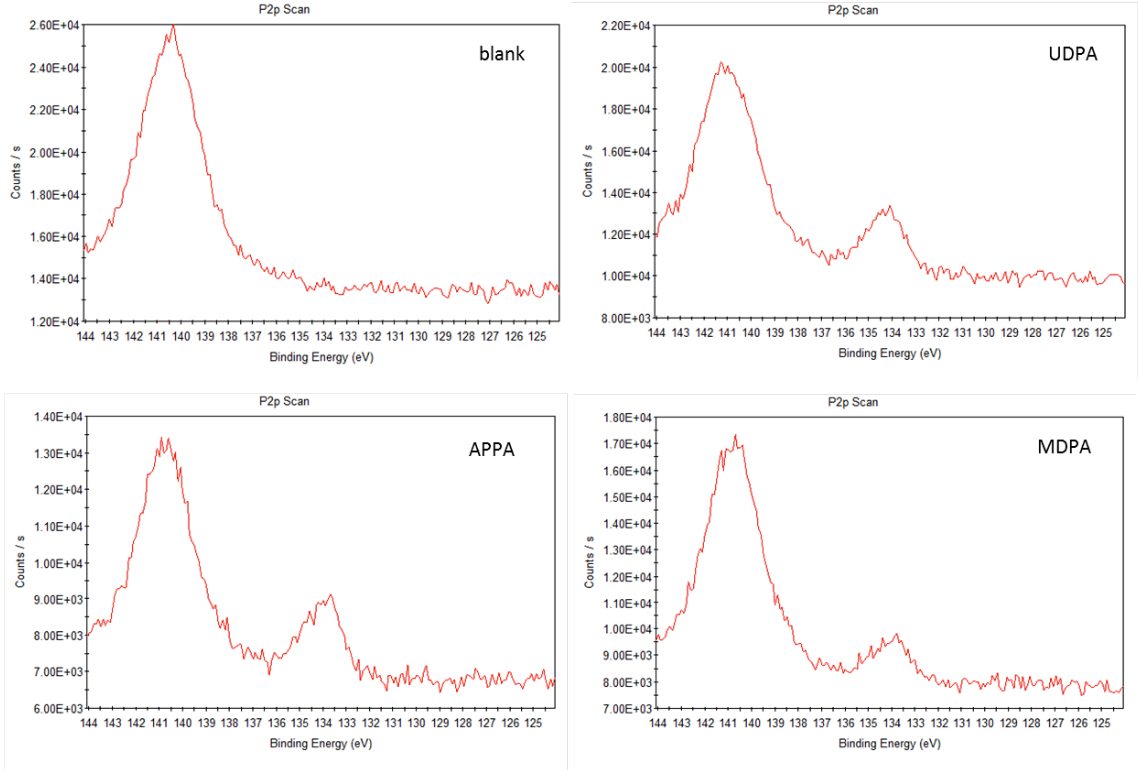


Figure 16. Comparison of the P(2p)-scans obtained from the zinc plated wires with different PA-coupling agents. The peaks at 134 eV correspond to the phosphor content on the surface of the sample.

Figure 16 shows peaks around 134 eV in the spectra of all PA modified samples, which can be attributed towards phosphor species present on the substrate surface. This peak does not appear in the blank, where no phosphonic acid was deposited. The peak at 141 eV is attributed towards Zn(3s). The atomic % of phosphor on the samples is shown in Table 13.

Table 13. Atomic % of phosphor on the measured samples.

Sample	P [%]
10-Undecenylphosphonic acid (UDPA)	2.3
(3-Aminopropyl)phosphonic acid (APPA)	0.9
12-Mercaptododecylphosphonic acid (MDPA)	2.7
blank	0

The results confirm, that phosphonic acid coupling agents can be deposited on the surface of the zinc plated wires and that they are still present after the second washing step and the temperature treatment. The (3-aminopropyl)phosphonic acid appears to be the least successful one, because of the low phosphor content found on the sample surface. Also, no nitrogen content > 0.5 atomic % was detected as shown in Figure 17 of the N(1s)-scans, however a small peak is indicated at 400.5 eV where the peak corresponding to nitrogen is expected.

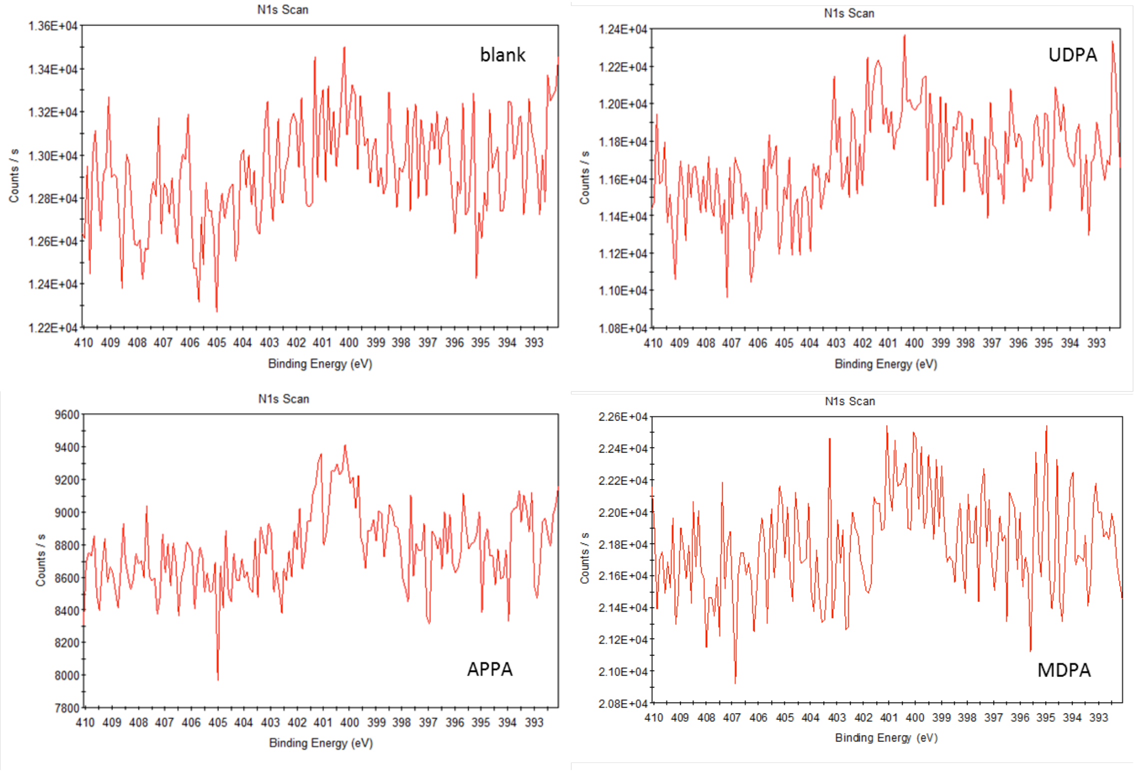


Figure 17. Comparison of the N(1s)-scans obtained from the zinc plated wires with different PA-coupling agents. At 400.5 eV the peak corresponding to nitrogen was expected. Nitrogen content >0.5 atom % was not detected on the APPA sample.

A possible explanation could be, that the short alkane spacer between the phosphonic acid and the amino groups result in a less dense packing of the monolayer. Due to the increased Van der Waals interactions between the longer UDPA and MDPA agents, the surface density of the monolayer is increased resulting in higher atomic% of phosphor on the surface of these samples [49].

In Figure 18 the results of the S(2p)-scans can be seen. The spectrum shows that sulfur is present at the surface of the MDPA coated substrate. This indicates that MDPA can successfully be adsorbed to the zinc oxide surface.

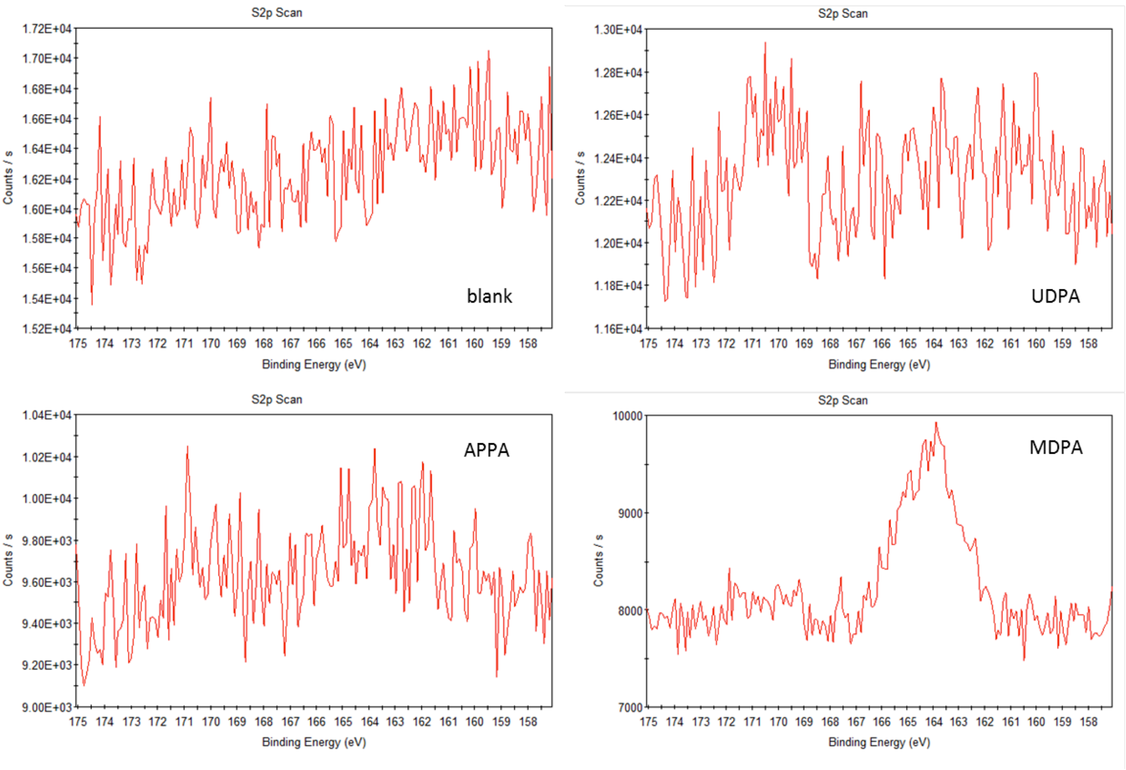


Figure 18. Comparison of the S(2p)-scans obtained from the zinc plated wires with different PA-coupling agents. The MDPA coated wire shows elevated amounts of sulfur on its surface as expected.

Comparison of SEM/EDX

The surfaces of the coated substrates were investigated using a scanning electron microscope. A ETD detector was used to measure the secondary electrons and a SSD detector was used to measure the backscattered electrons. The resulting images are shown in Figure 19and Figure 20.

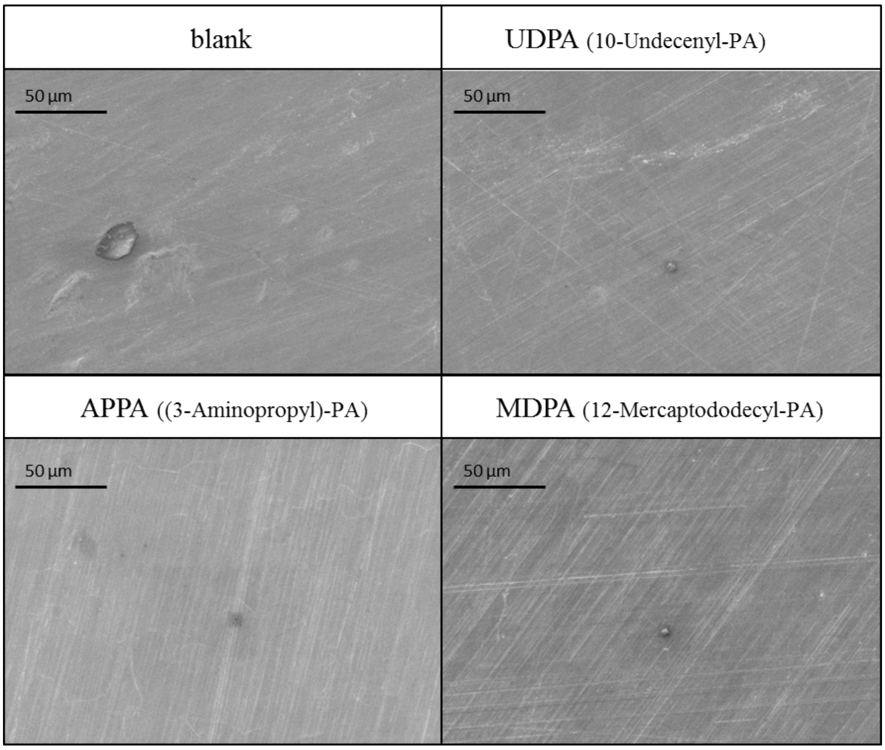


Figure 19. Images created by the secondary electrons from the zinc plates. No significant differences are visible between the differently coated samples.

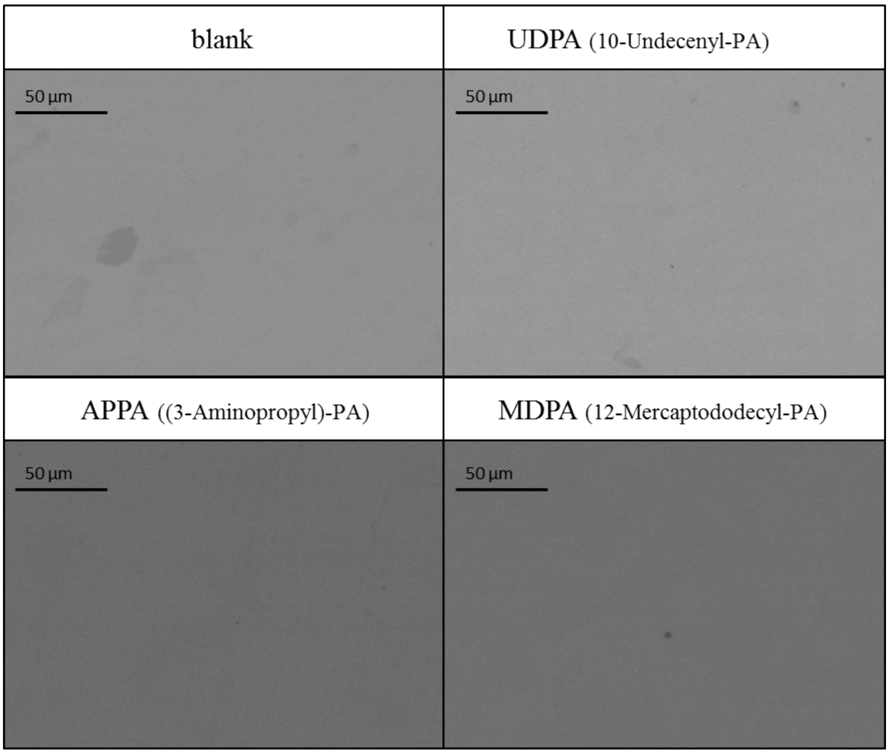


Figure 20. SEM images created by the backscattered electrons from the zinc plates. No significant differences are visible between the differently coated samples.

Neither the images of the secondary electrons, showing the topography of the surface, nor the images taken from the backscattered electrons, showing elemental differences, exhibit noticeable changes after the coating with coupling agent was performed. In the desired case molecular monolayers are attached to the surfaces, which would not be possible to see with this magnification. Also the elemental differences cannot be determined, since the electron beam penetrates the surface of the sample far beyond the monomolecular layer, overshadowing its signal with underlying zinc. Therefore, a characterization of the SAMs using SEM/EDX measurement is problematic and not advisable.

Reflectance IR-Spectroscopy

Coated APPA and UDPA samples were measured with IRRAS using uncoated zinc plates as background. Unfortunately no substantial spectrum could be obtained using this method. The scan count of 1000 was likely too low to provide viable information for monomolecular films. For further investigations measuring with a higher scan count is advisable to see if information can be gathered using this technique.

5.3 SQUALENE MODEL EXPERIMENTS

Squalene experiments were performed to mimic the behavior of the coupling agent coated wires during the vulcanization process with real rubber. Squalene is a liquid with a molecular structure similar to that of rubber. The wires were immersed in squalene mixtures with vulcanization additives and heated for 20 minutes at 160 °C. After the vulcanization is finished, the excess liquid squalene mixture can easily be removed from the substrate surface for further investigation. After the squalene experiments the samples were compared with each other. Also optical microscopy and SEM/EDX measurements were performed to gain insight to the changes of the zinc surface during the vulcanization process.

Optical comparison

In Figure 21 pictures of the zinc plates are shown before and after the squalene experiments were performed.

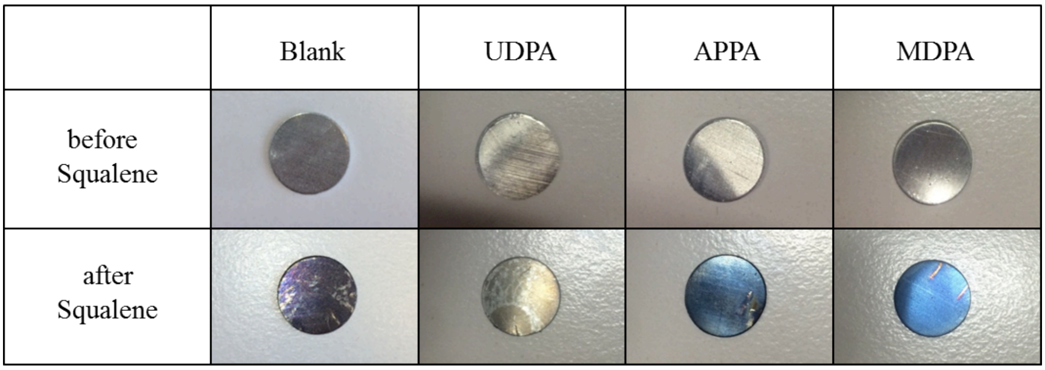


Figure 21. Pictures of the zinc plates after the squalene experiment.

All samples exhibit optical changes after the squalene experiment. Most of them also show changes of color. The different hues of blue stem from the cobalt salts in the squalene solution. In Figure 22 and Figure 23 optical microscope images are presented. Changes appear on all samples, also on the uncoated blank. However, it is hard to tell what the sources for them are and if this indicates better adhesion of the rubber to the surface.

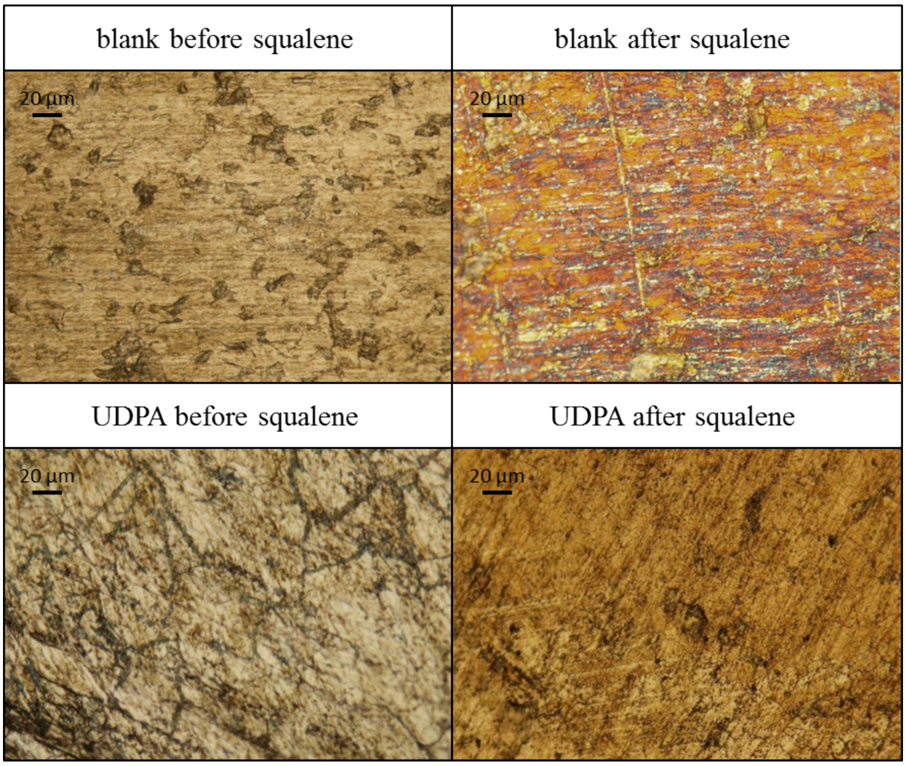


Figure 22. Comparison of the blank and the UDPA coated zinc plate before and after the squalene experiment was performed. Magnification: 600x.

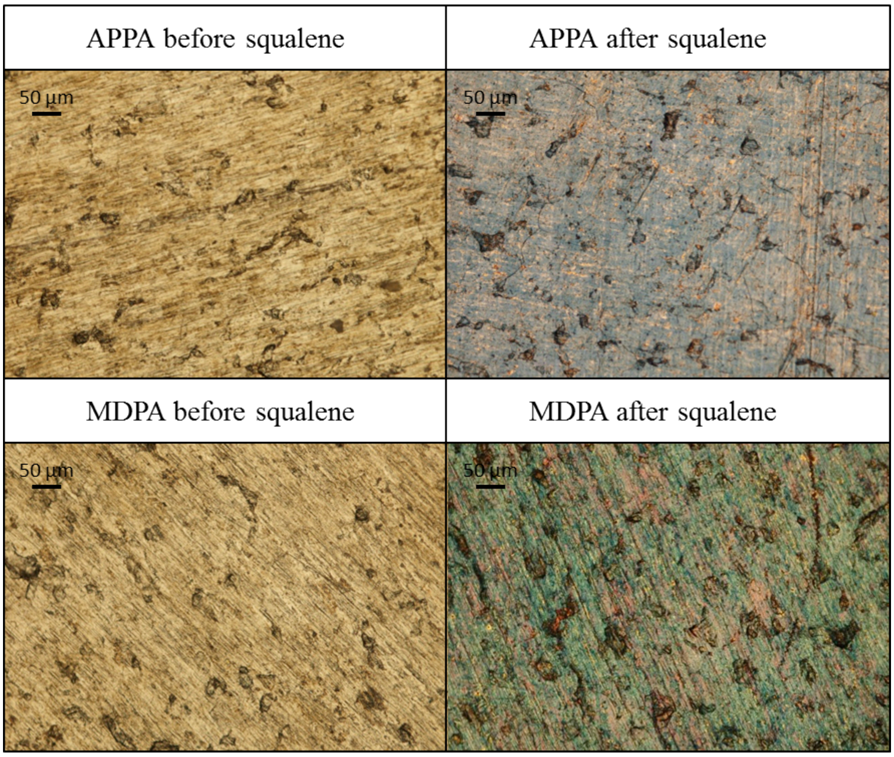


Figure 23 Comparison of the APPA and the UDPA coated zinc plate before and after the squalene experiment was performed. Magnification: 600x.

Comparison of SEM/EDX

After squalene experiments the samples were investigated using SEM/EDX measurements to gain further information about the topography of surface and their chemical composition. The resulting SEM images of the secondary electrons are presented in Figure 24.

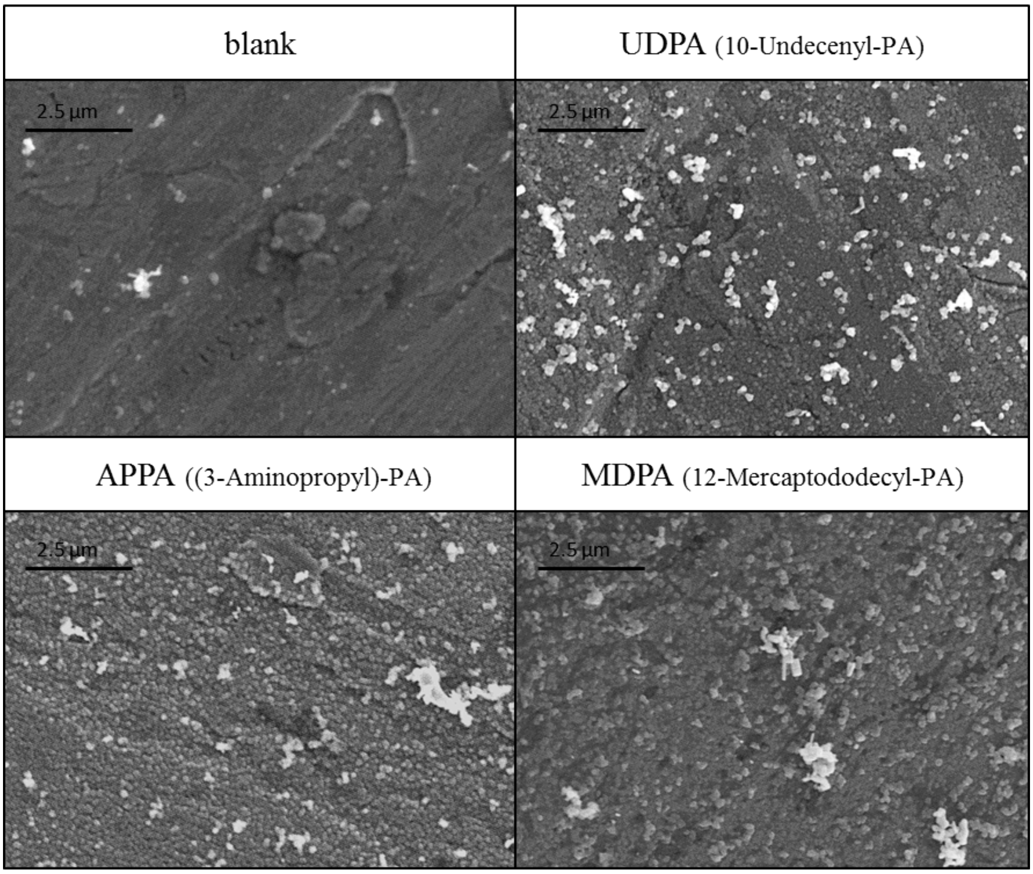
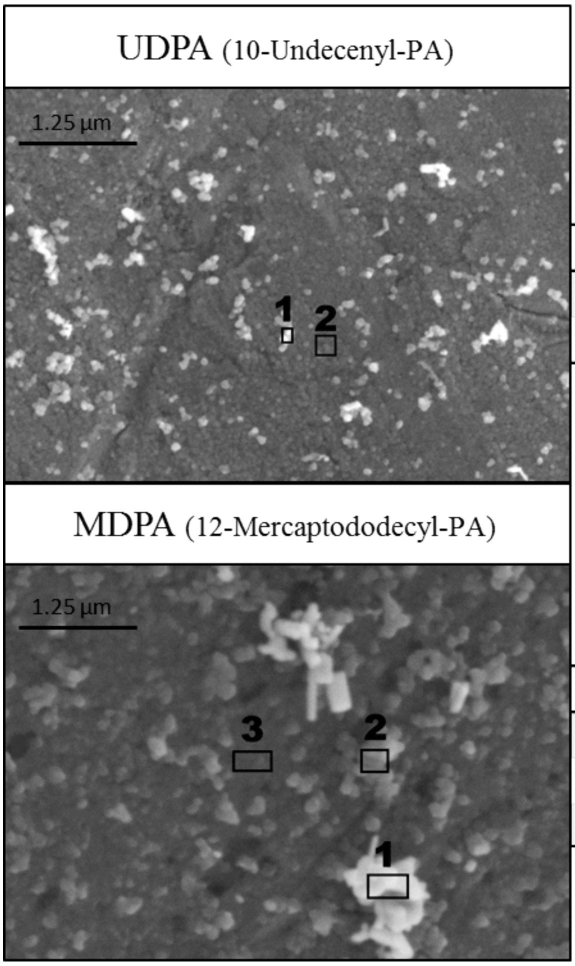


Figure 24. SEM images created by the secondary electrons from the zinc plates after the squalene experiments were performed. Magnification: 12000x.

There are noticeable differences between the samples. The blank appears to be smoother, and has less bumpy structures on the surface than its coupling agent coated counterparts. This means that the coating most likely influences the behavior during the vulcanization process. However it is unclear if the structures formed during the experiment result from a reaction with the zinc or if they are particles that adhere from the squalene solution.

Precise spot measurements revealed that the bright structures can be linked to zinc oxide particles or sulfur particles that adhere to the surface, or maybe even ZnS structures that formed during the sulfur vulcanization process with the zinc surface. as shown in Figure 25. The counts of the elements were normalized to the zinc and are shown on the right of the image.



Spot	Zn	C	O	S
1	100	5	11	17
2	100	1	5	3

Spot	Zn	C	O	S
1	100	15	32	13
2	100	20	19	46
3	100	13	13	17

Figure 25. Precise EDX measurements show, that the bright structures probably correspond to zinc oxide, sulfur or ZnS structures on the surface.

An overview of the samples was measured with EDX. The results were normalized to the zinc content and can be seen in Table 14. The blank, the UDPA coated and the AP-PA coated samples show very similar chemical compositions. This suggests that a similar reactions occurred or that similar particles adhered to the surface of the during the squalene experiments, resulting in unchanged chemical ratios.

Table 14. Overview of the elemental composition at the surface after the squalene experiment.

Sample	Zn	C	O	S
Blank	100	3	7	8
UDPA	100	3	6	10
APPA	100	3	6	11
MDPA	100	15	32	13

The composition of the MDPA coated sample however differs significantly from that of the others. The increase of the carbon content could be a result of squalene adhering to the surface. However, it is uncertain if the carbonaceous components really stem from chemically bound squalene. It is interesting to note, that the rough surface structure might also be a reason for more particles of the mixture to adhere to the surface. The elevated values could indicate that MDPA is able to act as an adhesion promoter for rubber on zinc. The elevated sulfur content could occur because of the higher amount of crosslinking sulfur found in the vulcanized squalene. The high level of oxygen might stems from immobilized zinc oxide powder or other oxygen species in the zinc oxide layer, or the carbonaceous layer. Generally, good interlocking of the vulcanized squalene and the MDPA-coated zinc oxide surface could lead to more immobilized organic residues in the matrix. This further suggests the increased oxygen value to be a sign for good adhesion properties between squalene and the MDPA coated zinc substrate.

In conclusion observations from the bare eye and the optical microscopy cannot give information about the physical and chemical structure of the metal surface. The SEM images show great differences in the surface structure of all coupling agent coated substrates while EDX data only reveal significant changes on the MDPA coated substrate after the squalene experiment. These experiments however only mimic the behavior of real rubber during the vulcanization process in lab scale and should therefore not be overvalued. Also, due to the penetration depth of the electron beam during the SEM/EDX measurements, as well as the uneven thickness of the structures on the substrate, the elemental composition represents only a rough estimation

5.4 RESULS USING REAL RUBBER SYSTEMS

To investigate the behavior in a technical environment, the treated zinc plated wires were used in NR, SBR and EPDM rubber systems. T-tests were performed to measure the strength of the adhesion between various rubber systems and the treated zinc plated wires. After the wires were embedded inside the rubber matrix, they were vulcanized for 20 minutes in a heated press. After the rubber was completely set, pull out forces were measured and the exposed wire surfaces were investigated using SEM/EDX and XPS.

5.4.1 PULL-OUT FORCES

To investigate the adhesion of NR, SBR and EPDM rubber to the zinc plated steel cords, pull out forces were measured a day after the vulcanization took place. The adhesion of NR and SBR was investigated by measuring 45 wires per coating. The same number of wires was used for measuring the blanks. The measurements include two batches of coated wires. For the first batch 30 wires were coated and for the second 15 wires were coated. The adhesion of EPDM rubber was investigates using 30 wires that were coated in a single batch. The results are shown in Figure 26.

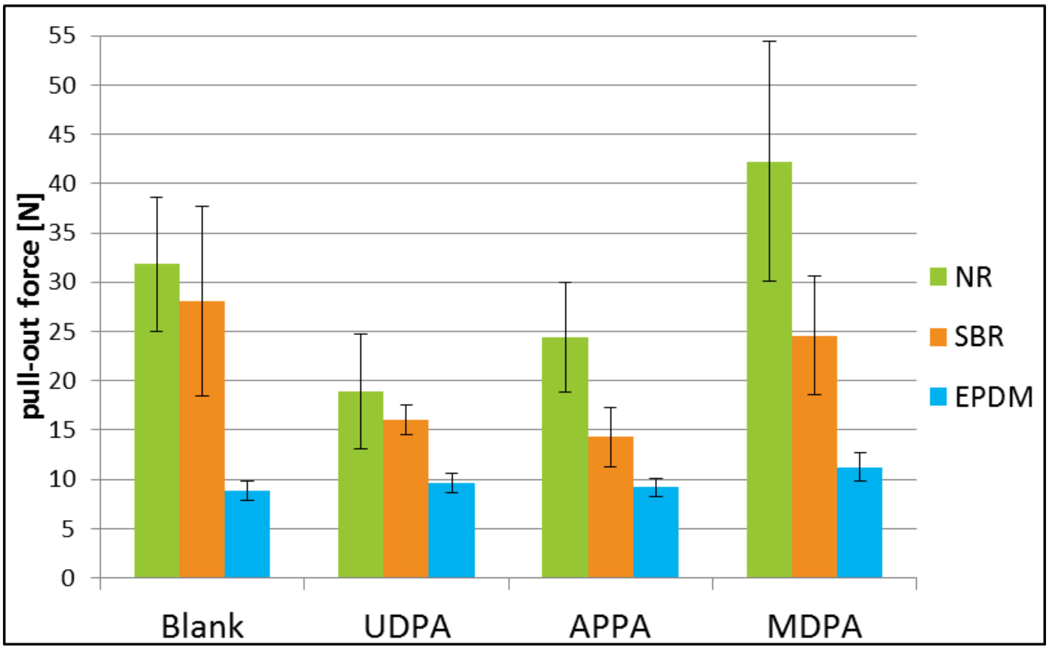


Figure 26. Pull out forces from different rubber systems and differently coated zinc plated wires.

All tested samples exhibit relatively low pull-out forces and coverages of 0%. For industrial usage at least 200 N would have been desirable, but those numbers could not be achieved with the tested coupling agents. To see if the processing of the rubber mixtures is responsible for the weak adhesion, the same NR and SBR mixtures were vulcanized on brass plated steel wires. Pull-out forces of around 170 N could be achieved for both rubbers when brass plated wires were used. This suggests that the rubber mixtures were able to be vulcanized, but show weak adhesion towards and the zinc plated wires.

NR

Compared to the blanks, only the MDPA coated wires could improve the adhesion of NR to them. Using UDPA and APPA coated wires lowered the adhesion of NR below that of the uncoated wires. The deviation of the pull-out forces, especially those from the MDPA coated wires, are relatively high which means that not all MDPA coated samples exceeded the uncoated blanks. Despite MDPA coated wires obtaining the highest adhesive values in our experiment, the pull-out forces of all samples are generally too low for industrial applications.

SBR

No coated wire could exceed the mean pull out force of the uncoated blank wire. MDPA coated wires again seem to have exceeded the adhesive power of UDPA and APPA coated wires. This was expected due to the known compatibility of mercapto coupling agents towards NR and SBR which UDPA and APPA are missing. Generally, the pull-out forces from the SBR rubber are lower than those of NR.

EPDM

EPDM exhibits the lowest adhesion to the wires. MDPA again exhibits the best results of all coupling agent coated wires. APPA coated samples were expected to show better results due to their compatibility towards EPDM rubber, but while having the lowest pull out forces, the values of all samples are very close and do not significantly differ when the deviations are taken into account.

5.4.2 COMPARISON OF SEM/EDX OF THE EXPOSED WIRES

SEM/EDX measurements of the exposed wires, after the pull-out experiments, were performed. The two tested wires were vulcanized with NR and SBR rubber. Since there was no visible coverage of the wires with excess rubber and additional steps of rubber removal or degradation was performed. The resulting images are presented in Figure 27 and Figure 29.

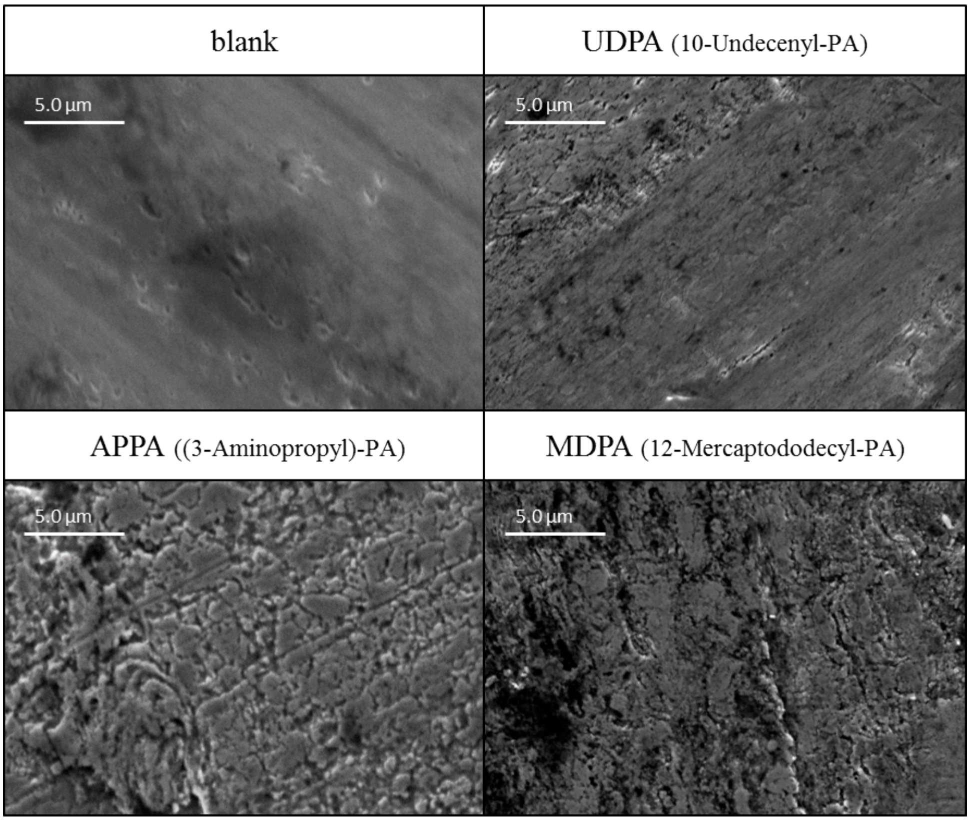
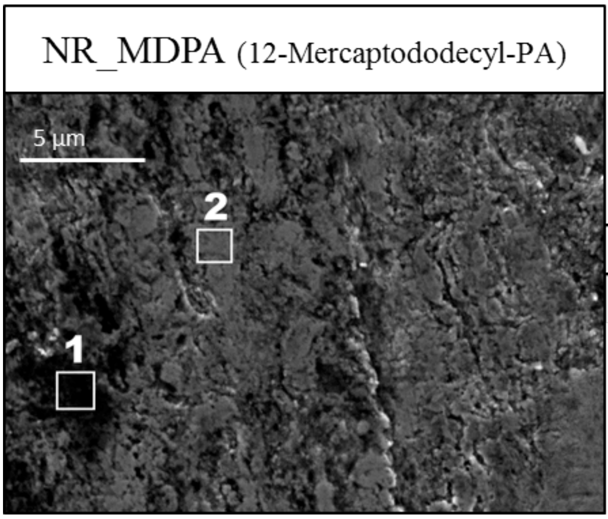


Figure 27. SEM images created by the secondary electrons from wire samples after they were pulled out of the vulcanized NR. Magnification: 6000x

The images of the wires after they were pulled out of the vulcanized NR rubber are shown in Figure 27 above. There are differences between the coated samples and the blank. EDX-measurements show, that the composition of the dark areas has a higher carbon, oxygen and sulfur concentration as shown in Figure 28.

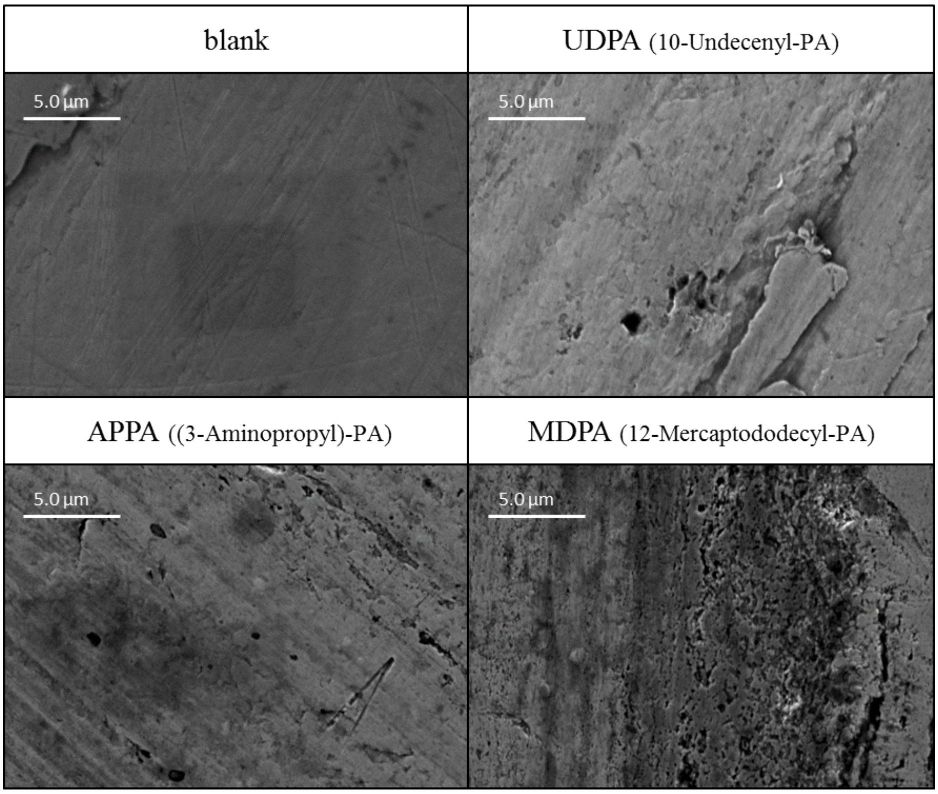


Spot	Zn	C	O	S
1	100	6	23	5
2	100	1	5	0

Figure 28. SEM images of the backscattered electrons showing differences of the elemental composition from the dark areas and the light areas of the MDPA coated wire, which was embedded in NR-rubber.

It appears as if most rubber adheres to the MDPA-coated wire. This would correlate with the relatively high pull-out forces of those wires observed after the vulcanization with NR (see Figure 26). On the other hand, pull out forces from NR were also strong with the uncoated blank, which shows very little dark spots on the SEM images.

It is possible, that areas or the wires in general, which were investigated, are not representative for the whole sample size. The relatively high variation of pull-out forces within the same sample group supports the hypothesis.



blank

UDPA (10-Undecenyl-PA)

APPA ((3-Aminopropyl)-PA)

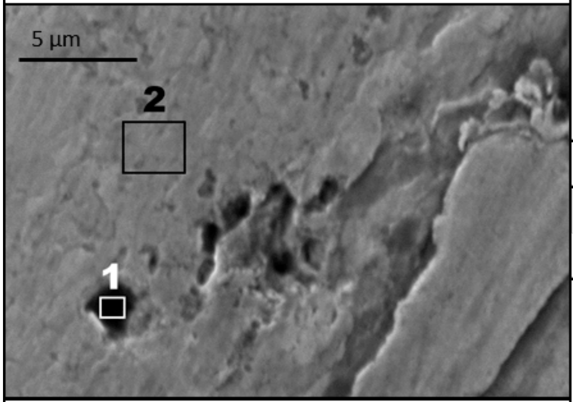
MDPA (12-Mercaptododecyl-PA)

Figure 29. SEM images created by the secondary electrons from wire samples after they were pulled out of the vulcanized SBR. Magnification: 6000x

EDX measurements again suggest dark areas to have a higher carbon, oxygen and sulfur content than the bright areas in the images as seen in Figure 30.

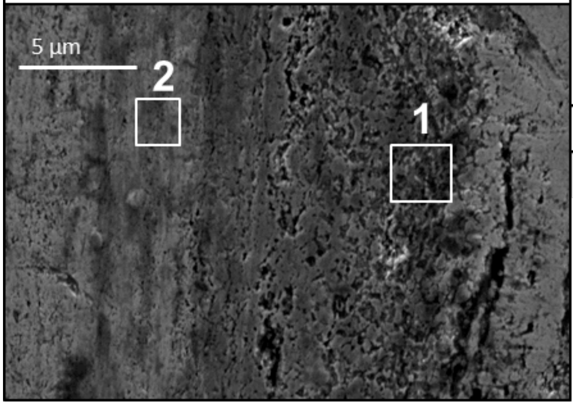
Also with SBR rubber, the least rubber seems to adhere to the surface of the uncoated blank, even though it showed the highest pull-out forces. The MDPA-coated wire however appears to have more rubber adhering to its surface compared to the other coated wires, which would correspond to the expected results based on the pull-out experiments. Finding a representative sample is a difficult task during SEM/EDX investigations. A higher number of measurements could make this a more viable method to investigate the substrate surface.

SBR_UDPA (10-Undecenyl-PA)



Spot	Zn	C	O	S
1	100	19	18	13
2	100	2	2	0

SBR_MDPA (12-Mercaptododecyl-PA)



Spot	Zn	C	O	S
1	100	4	19	2
2	100	2	2	0

Figure 30. SEM images of the backscattered electrons showing differences of the elemental composition from the dark areas and the light areas of the UDPA coated wire and the MDPA coated wire, which were embedded in SBR-rubber.

No dendritic structures are visible on the zinc plated wire surface after the vulcanization, especially when compared to the SEM images taken after the squalene experiments in chapter 5.3. But since physical interaction should not be the main reason for the bonding, the investigation of the interface layer via SEM/EDX is only suitable to a limited extend to characterize the adhesion of rubber to zinc using coupling agents.

5.4.3 XPS MEASUREMENTS OF THE EXPOSED WIRES

To investigate if the adhesion promoter layer sustains the vulcanization process, XPS measurements after the t-tests of the exposed wires were performed. The results show, that no phosphor could be detected on the metal surface of any sample. This suggests that the SAM on the wire does not withstand the vulcanization process and can therefore not act as a coupling agent. This explains the low pull-out forces of the samples shown in 5.4.1. Another possible reason for the SAM to be absent is that it is stuck to the pulled rubber instead of the zinc. This would mean that the pull-out process uncoated the metal from the coupling agent. However due to the low pull out forces, it is doubtful that enough force was involved to break the established P-O-Zn bond.

It is yet to prove that the vulcanization process is responsible for the loss of the SAM. It is possible that during the coating process, which derived from the standard procedure due to the high amount of wire needed, or due to the transportation of the samples, the SAMs could be damaged even before it was embedded inside the rubber.

6 SUMMERY AND OUTLOOK

The aim of this thesis was to investigate the spontaneous adsorption and binding of phosphonic acid coupling agents in the form of self-assembled-monolayers on zinc/zinc oxide surfaces to promote the chemical adhesion of rubber to the metal. The adhesion of rubber to metal is of great importance when specific reinforcement in rubber products is necessary and finding the right adhesion promoters is crucial to avoid fatal failures in the final product.

For this reason the three coupling agents 10-Undecenylphosphonic acid, (3-aminopropyl)phosphonic acid and 12-mercadodecylptophosphonic acid were investigated to shed light on the processing, the binding of them to the metal and the resulting adhesion strength

First, it was important to see, if the organofunctional phosphonic acids could successfully be bound to the substrate surface. Therefor contact angle measurements, XPS measurements, IRRAS measurements and SEM/EDX measurements were performed. The contact angle measurements show, that after the modification process was performed, the surface contact angles and resulting surface energies correspond with the expected results. This means, that the polarities of the surface decreased with the polarity of the head groups from the phosphonic acid coupling agents used, suggesting that a layer of adhesion promoter could be formed on the substrate. This is further supported by the XPS-measurements where phosphor was found on each surface of the coated substrates.

SEM/EDX proved to be unsuited to characterize the surface coating. The coupling agent consists only of a monomolecular layer, which the penetration-depth of the electron-beam surpasses making it not sensitive enough to receive conclusive information. Also IRRAS-measurements, despite their high sensitivity could not obtain meaningful spectra during our experiments. Maybe higher amount of scans is needed and should be investigated in further experiments.

Since coating parameters play a very big role in the process of forming well packed and strongly bound SAMs, the influences of the precursor concentration as well as the annealing parameters were investigated. It was shown, that the precursor concentration between 8.5 mmol/L and 53.5 µmol/L had little influence on the resulting coverage of UDPA on the substrate. The contact angles changed little, with changing concentration suggesting, that it is possible to process the samples with little amounts of coupling agent. By testing different annealing parameters with UDPA, contact angle measurements show that the coupling agent layers appear to be better packed when treated under inert atmosphere at 150 °C for 90 minutes.

Squalene experiments were performed to investigate the adhesion of rubber-like squalene on the substrates and the changes of the metal surface during the vulcanization process. Except for the UDPA coated sample, all zinc plates changed the color of the surface to a deep to dark blue, while UDPA became gray spotted in its appearance. SEM images showed an increased amount of bumpy, and flakey structures adhering to the surface of the samples coated with adhesion promoter. The EDX data suggests, that only MDPA coated substrates have an increased amount of carboneous species on the surface compared to the uncoated substrate. According to the squalene experiments, MDPA appears to be the most promising agent to promote the adhesion of rubber to the metal surface. This correlates with the results obtained with the t-tests. Generally, squalene experiments can only estimate the final rubber adhesion and cannot therefore replace tests, where real rubber is vulcanized onto the samples.

T-tests with NR, SBR and EPDM rubber mixtures were carried out to measure the pull-out strengths of the rubber-metal composites. As expected MDPA surpassed the other coupling agents in case of pull out force needed to extract the metal wire from the vulcanized rubber. Still it could not surpass the value of the uncoated blank with SBR rubber. In general, only low adhesion could be achieved with the highest mean pull-out value of 42 N for NR on MDPA coated wires and with the highest measured sample at 70 N. For industrial usage pull out forces of at least 200 N are usually necessary to guarantee adhesion that is strong enough to avoid failures. While the required adhesion could not be met in our experiments, further investigation is advisable to see if processing errors were responsible for the low adhesion between the rubber and the coated metal wires. We also advise tests on the stability of the phosphonic acid layers, to exclude the possibility that transportation time between the coating and the vulcanization did not play into account.

In summery the technology of bifunctional coupling agents brings great advantages. With this system rubber adhesion is not limited to physical adhesion alone and can be implemented on many metals like zinc. This thesis provides the basis for using the technique on zinc coated steel cords with phosphonic acid coupling agents. However further investigation and optimization will be necessary to shed light on the exact mechanism and to find a system that provides satisfying adhesion for competitive technical products.

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8 LIST OF TABLES

9 LIST OF FIGURES