PLASMA TREATMENT OF FIBROUS MATERIAL

SURFACE MODIFICATION OF REINFORCING CORDS FOR ADHESION PROMOTION TO RUBBER

André Louis

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Plasma treatment of fibrous material

Surface modification of reinforcing cords for adhesion promotion to rubber

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DISSERTATION

to obtain
the degree of doctor at the University of Twente,
on the authority of the rector magnificus,
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on account of the decision of the graduation committee,
to be publicly defended
on Wednesday the 6th of December 2017 at 12:45 hours

by

André Louis

born on the 30th of June 1981
in Nordhorn, Germany

This dissertation has been approved by:

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“A dream you dream alone is only a dream. A dream you dream together is reality.”

John Lennon

Für meine Eltern

To my parents

ACKNOWLEDGEMENTS

Writing this almost 6 years after the start of my Ph.D-project means, that a long lasting process has come to an end. It was a long journey, but looking back through these years, I can only state that the journey is indeed the destination. Without any doubt, this journey started already years ago in Osnabrück, where I studied for my Bachelor and Masters degree. Back in those days, I did not have the slightest comprehension, what an amazing journey with so many wonderful people from all over the world was ahead of me. I am deeply grateful for this wonderful time in my life. Nowadays I am working in a multi-national team and it is very clear to me, how well the time at the University of Twente prepared me for this job.

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Fabian, who were not just great colleagues, but became real friends over the years that I would not want to miss in my life.

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CHAPTER 1

Introduction:

Background, aim and structure of the thesis.

1.1 BACKGROUND OF THE INVESTIGATION

Composites made from rubber and reinforcing cords are very common and versatile materials. Well-known examples of products made from these materials are car- and bicycle tires, as well as several types of belts and hoses for a broad range of applications. The key element is the reinforcement by the cords that prevents large deformations of the rubber and, therefore, loss of the actual product function when high loads are applied in demanding situations. To guarantee this, high adhesive forces between the composite materials are necessary. A reinforcing effect is only achievable when the load forces can be efficiently transferred from the rubber to the cord. The better the interfacial bond within the composite, the stronger the material will be. In case of lack of adhesion, the cord will not contribute to the composite performance, as the rubber will deform while sliding along the cord, which cannot counteract the deformation. Because of this, adhesion between the reinforcing cord and the rubber matrix is important for the composite's performance.

Due to their chemical nature, polymeric cords and rubber are barely interacting. There is a lack of compatibility between the two phases that results in poor adhesion, which does not allow a proper reinforcing effect. In general, polymeric cords have a smooth and inert surface as well as a polar character. This holds true in particular for polyester and aramid cords. Therefore, the interactions with non-polar rubbers, which most industrially used rubbers are, are weak. The compatibility of both materials is important for reaching proper wetting of the cord with rubber, which is necessary for adhesion phenomena like surface and interface effects, mechanical interlocking and chemical bonding. None of the cords used for reinforcing applications are compatible with rubber without further treatment. Treatments of polymeric cords are performed in order to enhance the compatibility and to form a physical or chemical bond, which then provides adhesion between both components. The standard treatment in the tire industry is the Resorcinol-Formaldehyde-Latex (RFL) treatment, which is basically a dipping process for the cord to provide chemical adhesion to the rubber matrix.

The main function of the adhesive interface is to transfer the load stress from the rubber matrix to the reinforcing cord. One of the first reinforcing materials for rubber was cotton [1]. Its filaments served as anchoring points within the rubber. When a load is applied, frictional forces must be overcome to pull out the cotton; the larger the interface, the higher the required forces. The application of adhesive chemicals started shortly after, and the RFL-system became the industrial standard.

Its name stands for the general concept of using a RF-resin that bonds to the cord and a latex phase which vulcanizes with the rubber. In fact, there are many variants of this concept adapted to the individual polymeric cords and their applications. While this system works very well in terms of product performance, it uses toxic ingredients and requires a complex and energy intensive treatment process. Because of these drawbacks, the search for possible alternatives has been a challenge always since the introduction of the RFL-system.

Plasma treatment, which uses a highly energetic gas, has been used for adhesion promotion in a great variety of industrial applications with increasing success. Either as a preparation step before the application of a chemical adhesive or as a stand-alone treatment. Therefore, the idea to use it as an alternative to RFL is a logical choice. The approach how to promote the adhesion between polymeric cords and rubber by plasma treatment in the present work is new and inventive.

1.2 AIM AND STRUCTURE OF THE INVESTIGATION

The aim of the present work can be split into two categories:

1. The design of a plasma treatment line which is suitable for handling polymeric reinforcing cords;
2. The investigation how to establish a chemical bond between the reinforcing cords and rubber.

The design part begins with the general concept of the plasma line. What kind of plasma equipment should be used and which ancillary equipment is needed? The starting point is a rather simple setup for basic trials. Over time the plasma line is developed stepwise into a highly sophisticated and specialized compilation of different types of equipment. This development and the crucial stages are documented and discussed, and the required finetuning of the assembly to reach the best possible adhesion is described. The questions which have to be answered during the R&D trajectory of the plasma treatement line are:

- How long should the cord be exposed to the plasma?
- What kind of plasma gas is the most suitable?
- What process atmosphere is best for the treatment procedure?
- Do the polymeric cords have to be decontaminated before the actual plasma treatment?
- How to handle the freshly treated cord?

In fact, the aim of this part of the work is to develop a complete plasma treatment line for single cords on a Technology Readiness Level of 5 to 6: the validation or demonstration of this technology in a relevant environment. The goals concerning this technology are to understand what makes it suitable for the cord and how to achieve the best adhesion; besides, a stable and robust process has to be developed.

At the same time as the equipment of the plasma line is developed step by step, also the question how to create chemical bonds between both materials has to be investigated. The aim here is to understand what kind of moieties are needed on the surface of the cord, thus what chemicals are required and how do they provide adhesion. Also for the chemical part the approach is twofolded. On the one hand, adhesion promotion is closely connected to the generation of hydroxyl groups to increase the polarity and thus the compatibility with adhesives. This path is followed in this work as well, but here with the aim to make the cord surface reactive towards special additives which at a later stage can react with the rubber to form chemical adhesive bonds across the interface. On the other hand, prevention and masking of the hydroxyl groups will also be investigated. The hypothesis behind this is, that the polarity of hydroxylic functional groups hampers the compatibility of the cord surface towards rubber. Therefore, the aim within this part is to understand, if a plasma coating which decreases the polarity can enhance the actual compatibility between both materials. Besides, it will be studied if establishment of a chemical bonding promotes adhesion when a suitable precursor, which is injected into the plasma stream, is applied. The other group of precursors, as described above, decreases the polarity of the cords and enhances compatibility to the rubber. The difficulty hereby is, to find a precursor which creates a hydrophobic surface and at the same time provides functional groups which can react with the rubber. The approach in the present work is to apply sulfuric precursors that create moieties on the surface, which can interact with the sulfur complexes that are created by the curing agents of the rubber during vulcanization, and can form covalent bonds from the cord to the rubber.

1.3 CONCEPT OF THE THESIS

After this introduction, the current state of the art of reinforcing cords and the technologies to achieve adhesion to rubber will be reviewed in Chapter 2. The industrial standard for adhesion promotion: RFL coating, is described in detail and several possible alternatives are explored. Furthermore, the term plasma is introduced and it is explained how it can be used to modify surface properties. Industrial plasma equipment is reviewed and the state of the art for adhesion promotion with the plasma technique is discussed.

In Chapter 3, the concept and development of the plasma treatment line used for the experiments in this work are described. The general setup is described, and the plasma devices as well as the peripheral equipment are explained in detail. The development of the plasma line during the experimental phase is documented including the introduction of new additional equipment and adjustments, which became necessary from the lessons learned during the experiments.

The following Chapter 4 covers one of the chemical approaches that were applied to promote adhesion between the reinforcing cord and rubber. The chemicals being used for the experiments described in this chapter all contain sulfuric moieties in their molecules. Using sulfur for adhesion promotion and the requirements to successful apply these chemicals in the plasma treatment process are described here.

In Chapter 5, another approach is taken. Instead of sulfur, the focus is on silanes and how to use them for adhesion promotion. This is a very interesting novel concept of adhesion promotion between reinforcing cords and rubber. Besides the chemicals being used in the plasma treatment process, also different routes of applying silanes to the cords are studied.

The interfaces between the plasma treated reinforcing cords and rubber are investigated and compared to the industrial RFL standard in detail in Chapter 6. This is of interest, as it allows for understanding the differences in force transmission between both materials, depending on the technology used to achieve adhesion. Another topic in this chapter is the improvement of rubber penetration into the cord filaments structure of the plasma treated cords and the effect on adhesion.

In Chapter 7, the effects of plasma on the actual cord properties are investigated, which is of interest as the plasma flame reaches temperatures of several hundred degrees Celsius. It is analyzed how the plasma immediately affects the properties and if those effects are temporary or permanent. Furthermore, the ageing of treated cord material as well as of vulcanized test samples is studied in order to understand how the plasma treated samples perform over a longer period of time.

Finally, the present thesis is summarized in Chapter 8, which reviews the achievements and answers the research questions described above.

CHAPTER 2

Literature survey:
Adhesion of cords to rubber compounds
and
plasma technique

This chapter defines the problem statement and explains, why reinforcing cords require a treatment to be able to adhere to rubber. The standard treatment method is explained in detail. Alternatives are introduced and the advantages and disadvantages over the existing standard are discussed. Finally, an in-depth introduction into plasma treatment is given, and the state of the art with respect to this technique is reviewed.

2.1 INTRODUCTION

Composites made from rubber and reinforcing cords are very common and versatile materials. Well-known examples of products made from these materials are car- and bicycle tires, as well as several types of belts and hoses for a broad range of applications. The key element is the reinforcement of the composite product with cords to prevent large deformations of the rubber and, therefore, loss of the actual product function when high loads are applied in demanding situations. In order to do so, sufficiently high adhesive forces between the composite materials are necessary. A reinforcing effect is only achievable if the load forces can efficiently be transferred from the rubber to the cord. The better the interfacial bond within the composite, the better the product properties will be. In case of lack of adhesion, the cord will not contribute to the composite performance, as it will simply slip in the rubber matrix with only minor work required.

The complexity of such a rubber composite construction is shown in Figure 1, which represents a schematic drawing of a passenger car tire. In this example, several reinforcing elements can be found: the carcass layers (4,5), the bead (6), the belt layers (8) and the cap ply (10), which in this example is called Nylon overhead.

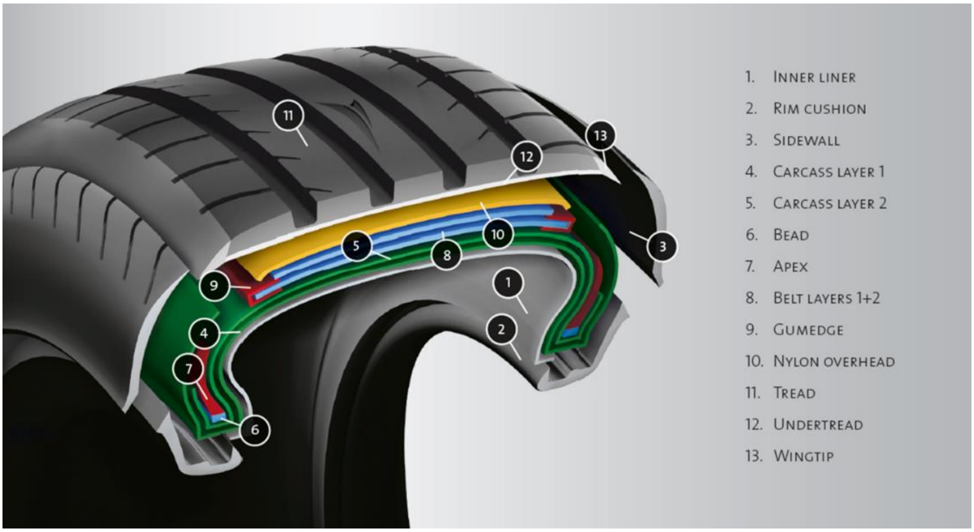


Figure 1: Cross section of a typical passenger car tire [1].

2.1.1 Reinforcing cords in tire construction

There is more than one type of reinforcing material used in a tire. In general, they can be divided into two categories:

- Steel cords
- Polymeric cords

The main reinforcing materials are shown in Table 1. Steel as material for reinforcing cords provides superior tensile strength and modulus properties as well as temperature resistance, but also features the disadvantage of a very high density which makes the composite heavy.

Table 1: Radial tire reinforcements – Main materials and their properties [2].

Material (filament or cord)	Density (g/cm³)	Tensile strength (N/mm²)	Tenacity (cN/dTex*)	Modulus (N/mm²)	Specific Modulus (cN/dTex*)
Steel	7.86	3300	4.2	200000	254
Polyester	1.38	1076	7.8	5934	43
Polyester (HMLS)	1.38	1035	7.5	7728	56
Rayon	1.51	785	5.2	14747	98
Polyamide	1.14	923	8.1	2964	26
Aramid	1.44	2952	20.5	73440	510

***cN/dTex: centinewton / 1 gram per 10.000m cord**

Polymeric reinforcing cords feature in general lower mechanical properties than steel except for aramid cords, which show an excellent performance. If the specific weight of the polymeric cords is considered, their performance is on a more competitive level or even superior in case of aramid.

The type of reinforcing material to be used depends strongly on the reinforcing element within the tire and for what kind of application the tire is produced. As can be seen in Table 2, the bead of a tire is always made of steel. The bead ensures that the tire will stay on the rim under all circumstances and, therefore, steel is used in this case. Besides this part of the tire, the materials used are much more diverse.

Still, if the weight of a tire is less important and robustness is one of the key features, like for truck tires, mainly steel will be used.

Table 2: Radial tire reinforcements – Application roadmap [3].

Application	Bead	Carcass	Belt	Cap ply
Motorcycle	Steel	Polyester, Rayon, Polyamide	Steel, Polyamide, Aramid	Polyamide, Aramid
Passenger cars	Steel	Polyester, Rayon, Aramid (Racing)	Steel	Polyamide, Aramid, Polyester
Light truck	Steel	Polyester, Rayon, (Steel)	Steel	Polyamide, Aramid, Polyester, (Steel)
Truck & Bus	Steel	Steel	Steel	Steel, Polyamide, Aramid
Industrial	Steel	Steel	Steel	Steel, Polyamide, Aramid
Agricultural	Steel	Polyamide, Polyester, Rayon	Polyamide, Polyester, Rayon, Steel	Steel, Polyamide, Aramid
Earthmover	Steel	Steel	Steel	Steel, Polyamide, Aramid
Aircraft	Steel	Polyamide	Polyamide, Aramid	Polyamide, Aramid

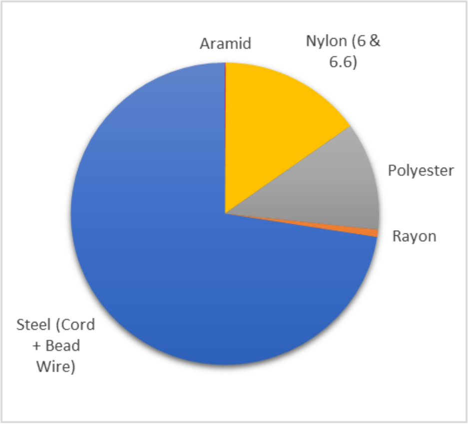
In the case of passenger car tires, where features like robustness and heavy loads are less important, but a lower tire weight and price are significant, the use of polyester and rayon for the carcass layer of the tire are common. The cap ply layer is usually made of polyamide 6 or 6.6. Aramid is used for high performance tires and in particular for racing tires, where superior mechanical properties and low weight are very important, and the price of the tire is less significant. The same situation applies to tires used for airplanes, where even the carcass layers are made of polyamide.

Table 3 illustrates the amount of reinforcing materials used in the year 2013. In total, 6316 kton of cords were used in the tire industry worldwide. Roughly three quarters of it, in numbers 4580 kton, was steel cord or bead wire. The remaining 27,5 % were covered by polymeric material. The largest stacks in this category were the polyamides with 950 kton, followed by polyesters with 730 kton. A much smaller contribution was held by rayon (50 kton) and aramid (6 kton).

Polyamide 6 is widely applied for cap ply purposes and in combination with steel cord for the belt layers of a tire. It is less applicable for the carcass due to its low modulus (see Table 1) and its low glass transition temperature (T_g), that is as low as 50 °C. Polyamide 66 has similar disadvantages and is mostly used in passenger car tires in India and South America [4]. However, polyamide is used for aircraft tires, as it makes it possible to keep the tire weight low due to its very low density.

The second most used polymeric material is polyester. It also suffers from a relatively low T_g of about 69 °C, but it features a high modulus and high tensile strength. These high mechanical properties are counteracted by a significant amount of shrinkage and the rather inert surface that hinders chemical or physical interactions and, therefore, results in low adhesion properties compared to polyamide or rayon cords.

Table 3: Reinforcement material used in tires in 2013 [5].

Material	**2013 Worldwide Sales (in kton)**	
Aramid	6	
Polyamide 6 & 6.6	950	
Polyester	730	
Rayon	50	
Steel (Cord + Bead Wire)	4580	

Rayon has been one of the first reinforcing materials on the market and also the first half-synthetic cord back in 1930. Its properties were sufficient for that period, but due to a more demanding development of the tire market, the properties were significantly improved later on. A critical aspect of rayon is, that it has a hydrophilic nature and takes up moisture from the environment. The uptake is in the range of 7 w% and causes a strong loss of mechanical properties.

The properties of aramid shown in Table 1 are clearly superior over the other polymeric materials. However, while the very high modulus and tensile strength are significant advantages, they are accompanied by very low elongation at break values. This can be a problem for the following reason: when several layers of aramid are used in a tire construction, the outer layer causes a compression deformation of the inner layers [4]. Under these circumstances, the aramid performance is poor. The problem can be reduced by applying a large twist factor to the aramid cord. Furthermore, aramid has a highly inert surface too, which results in only little interaction with rubber without further treatment.

2.1.2 Adhesion mechanisms

The adhesion between the reinforcing cord and the rubber matrix is, as already mentioned, of significant importance for the composite's performance. As both categories of reinforcing materials differ fundamentally in their chemical nature, their adhesion mechanism with rubber will also be entirely different.

Steel cords obtain adhesion to the rubber phase via mechanical interlocking that is formed due to a redox reaction of Copper (Cu), Zinc (Zn) and Sulfur (S). During production, the steel cord is coated with a Cu layer, followed by a Zn layer. Then a diffusion process is applied to the cord that allows these coated layers to form a brass layer. Oxidation causes the brass layer to separate on the surface again. Consequently, a layer of ZnO is established with a number of Cu atoms in it. The Cu diffuses to the surface and forms on top of the ZnO-layer a thin Cu_2O coating. In contact with the rubber compound containing sulfur, a redox reaction is taking place during vulcanization, causing the growth of dendritic Cu_xS mushrooms on the cord surface. While the rubber is curing, a tight mechanical interlocking is established providing the desired adhesion between steel cord and rubber matrix.

Polymeric cords and rubber are not very well adhering as there is a lack of compatibility between them. In general, polymeric cords have a smooth and inert surface as well as a polar character. This holds true in particular for polyester and aramid cords. Therefore, the interactions with non-polar rubber are weak. The compatibility of both materials is important to enable a proper wetting of the cord with rubber, which is necessary for adhesion phenomena like surface effects, mechanical interlocking and chemical bonding. None of the cords used for reinforcing applications feature a compatibility with rubber which is sufficient without a treatment. Because of that, a treatment of the polymeric cord is performed in order to enhance the compatibility and form a physical or chemical bond, which provides a proper adhesion between both composite components. The standard treatment in the tire industry is the Resorcinol-Formaldehyde-Latex (RFL) treatment, which is basically a dipping process for the cord to provide chemical adhesion to the rubber matrix.

2.2 STANDARD RFL TREATMENT FOR ADHESION PROMOTION OF POLYMERIC CORDS

Rubber articles used in demanding applications are commonly reinforced rubber/cord or rubber/steel composite materials. The reinforcement effect comes from the combination of these two very different materials: on the one hand a highly elastic, but low strength rubber and on the other hand a cord with high strength and very low elongation properties. The adhesion between both components of the composite is thereby the critical parameter for gaining the maximum overall performance from such a composite material. The main function of the adhesive interface in this composite is to transfer the load stress from the rubber matrix to the reinforcing cord. One of the first reinforcing materials for rubber was cotton and the only treatment necessary was to dry it. That was sufficient, because fibers made from cotton are not smooth and the filaments are sticking out of surface [4]. These filaments can be used as anchoring points within the rubber and if a load is applied, frictional forces have to be overcome in order to pull out the cotton. The use of adhesives started shortly after. A blend of casein and natural rubber latex was the first adhesive system, which gave acceptable levels of adhesion for rayon [6]. The introduction of improved rayon cords and full-synthetic cords like polyester, led to increased adhesion requirements and, therefore, to the development of new adhesives. One of these new developments at that time was the RFL system, which quickly became an industrial standard and still is since 1938. The RF resin provides bonding to the cord and the rubber-like latex component bonds to the rubber by co-vulcanization. The term RFL-treatment covers a large variety of treatments. They share the same technique but differ in recipe and application. This implies that the system is adjustable for various combinations of materials used for specific composites, as each cord and rubber may require optimized treatment conditions.

The production of a RFL adhesive dip is done in two steps. A typical recipe for such an adhesive dip is shown in Table 4. In a first step, resorcinol: see Figure 2, is dissolved in water to obtain an aqueous solution. Subsequently, formaldehyde and sodium hydroxide as condensation catalyst, are added to the solution. The addition of sodium hydroxide makes the solution alkaline. The mixture has to mature for about six hours at room temperature. During this maturation phase a slow condensation reaction is taking place and methylol groups (resoles) are formed which further condensate and form resins of a low molecular weight. The maturation phase is stopped when the resin reaches the desired molecular weight and the viscosity is still very low.

Table 4: Common formulation of RFL dip system for rayon cord [7].

Component	Parts (wet)	Parts (dry)
Resorcinol	9.4	9.4
Formaldehyde (37 %)	13.8	5.1
Sodium hydroxide (10 %)	7.0	0.7
Water	157.8	-
VP latex (40 %)	212.0	84.8
Water	100.0	-
TOTAL	**500.0**	**100.0**

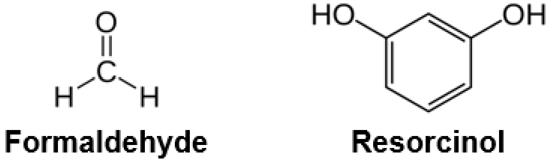


Figure 2: Molecular structures of formaldehyde and resorcinol.

The second step is the introduction of a latex solution. Under gentle mixing, the resin is added to the latex to ensure good mixing of the dip system [6]. Finally, the dip solution can mature for 24 h before further use [7]. The final dip properties are shown in Table 5. An increase of formaldehyde concentration also increases the rate of methylol formation. The optimal formaldehyde to resorcinol ratio is between 1,5:1 and 2:1, which results in a complete methylol reaction. Furthermore, the formaldehyde concentration also increases the viscosity of the resin because of the formation of higher molecular weight products [6]. The best resin/rubber ratio is between 5:1 and 7:1. Within these ratio regions, a fine-tuning of the RFL dip is possible. However, often a standard formulation is used that provides sufficient adhesion for a wide range of cord/rubber combinations to simplify production procedures. The type of latex can also be optimized for a specific composite, but commonly a styrene/butadiene/vinyl pyridine (VP) terpolymer latex is used [7].

Alternatively, the two-stage preparation of a RFL dip can be replaced by another method which combines both stages to a single production step. That method has two significant advantages [7]:

- Greater control over the condensation reaction,
- Dip has a much-improved shelf life.

The exothermic characteristic of the condensation reaction can cause a too rapid conversion of resorcinol and formaldehyde into resin. When this happens, the resin turns into an entirely solid state before the actual valid condensation time has been reached. This cannot happen in one stage mixing, because the heat of the exothermic reaction is distributed into the latex phase as well and can be much better controlled. Besides, the one stage preparation gives significantly more freedom to store the RFL dip for a certain time. Instead of hours of time to apply the dip in case of the two-stage mixing, the dip prepared in one stage can be stored up to three weeks. Another advantage is, that one stage mixing forms a much more intimate dispersion of the ingredients and, therefore, forms an interpenetrating network of resin and rubber phase.

Table 5: Final dip properties of a typical formulation [6].

Properties	Value
Dip solids (%)	18-26
pH	9 to 10
Formaldehyde/resorcinol molar ratio	2/1
Resin/latex ratio	15-20/100

Another alternative method uses a pre-condensed novolak resin (penacolite) instead of forming a resin from resorcinol and formaldehyde. It is an acid-catalyzed resin with a molecular weight of around 300 g/mol [4] dissolved in water. The solution has a resin content of around 70 %, which makes it highly viscous and it is also strongly acidic with a pH value of around 2.0 [7]. Dilution is required to reduce the viscosity, and to increase the pH of the solution to a value higher than 8.5, which prevents coagulation of the latex, ammonia is added. Formaldehyde is still necessary and is slowly incorporated under gentle stirring to the latex/resin solution. This completed dip is then allowed to mature for at least 18 hours before use. Like the single step preparation process, this novolak based dip can be on shelf for an extended amount of time.

The next step is the application of the dip on the cord. Simply spoken, this is done via an immersion of the cord in a bath of the RFL dip. However, as can be seen in Figure 3, such a setup is rather complex. In this example, the cord enters the process on the right and is leaving it on the left. The cord is taken from the feed rolls that have several kilometers of cord on them. Through the entry nip the cord is forwarded to a buffer system called entry accumulator. In case that the feed roll runs empty, the buffer prevents a down time of the whole treatment line. The cord then enters a number of rolls which have a relative lower velocity to the main drive. These hold back rolls are used to control and maintain a certain tensile stress on the cord during processing. Depending on the cord, one or two impregnation steps must be applied, where the first one is a pre-dip and the second one is the actual RFL-dip. Nevertheless, the impregnation procedure is similar in both cases. In a first step, the cord is immersed in a bath to take up the dip. The actual amount of dip pick-up can differ with respect to the cord. Subsequently, a dip pick-up control system follows. Here the removal of excess dip from the cord surface is executed. Often this is done by a squeeze roll, alternatively a vacuum unit or a beater are used.

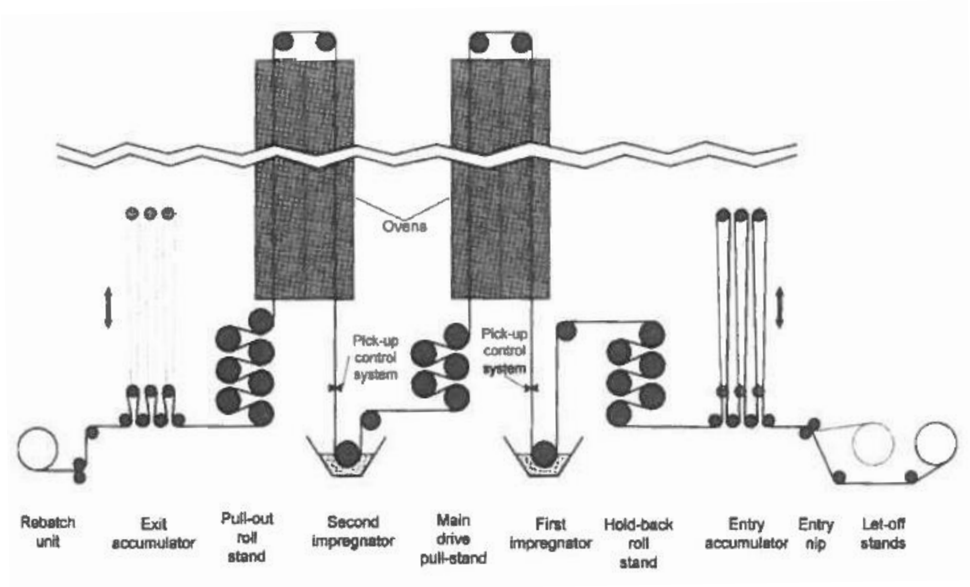


Figure 3: Setup of an industrial two dip system for polymeric cords [4].

The cord then enters into an oven, where it is dried and the resin gets fully cured. A second smaller buffer called exit accumulator is used, which is installed just in front of the re-batch unit that winds up the cord on a feed roll. Such a process comprises several process parameters: Next to the chosen materials and dips, the cure temperature and the residence time are the most important ones. The temperature in the oven varies from 130 ºC to 225 ºC and the residence time is commonly between 15 and 20 seconds, but can be as long as 2 minutes. The residence time can be changed with the cord speed or the number of loops of the cord in the oven. Another parameter is the tensile force applied to the cord.

The chemical reaction between the resin molecules of the RFL itself as well as the reaction with the cord is initiated by heat which is provided from the ovens during the dipping process. Figure 4 shows an example of such a reaction, where a resole-group of the resin reacts with a polyamide group of a nylon cord. The hydrogen atom attached to the nitrogen atom of the polyamide group is responsive to the hydroxyl group of the resole. A condensation reaction takes place which is driven by the elevated temperatures. Via this reaction pattern covalent bonds between the cord and the resin of the RFL dip are formed. Additionally, the resin of the RFL coating is also fully cured using the remaining formaldehyde molecules from the preparation of the RFL dip.

In the case of rayon, a single treatment with a RFL dip is sufficient, as the reactivity of the cellulose-based cord is high enough and doesn’t require any pre-dipping procedure. The reaction of rayon differs from the example of polyamide shown in Figure 4 before. In this case, the hydroxymethyl groups of rayon undergo a condensation reaction with the formaldehyde like the reaction pattern of the RFL resin itself. For rayon cords with low toughness, up to 70 % of the Vinyl-Pyridine (VP) latex content can be substituted by a standard SBR latex. Rayon cords with high toughness and high wet strength need a VP latex content of 60 to 80 % in order to provide good adhesion, but this kind of rayon cord is mainly used in the textile industry [6]. The dipping process is straight forward, as the rayon cords are dipped in the RFL, and the impregnated cords with the deposited layer are dried and cured by exposure to heat. Commonly a treatment time of 1 to 2 minutes at a temperature range between 130 ˚C and 150 ˚C is sufficient to achieve good adhesion levels. The adhesion is not only based on chemical bonding at the interface between dip and cord, though that is the major contribution. Also, mechanical and physical interactions contribute to the overall adhesion effect.

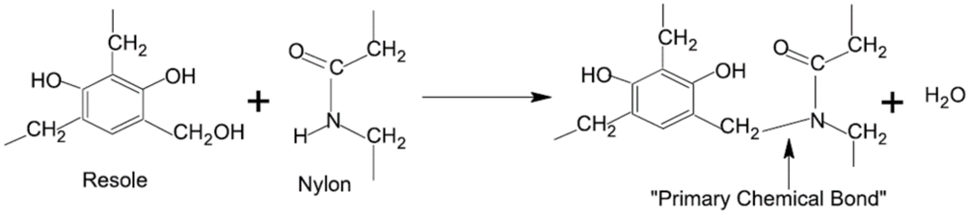


Figure 4: Condensation reaction scheme of resole and polyamide (nylon) forming a covalent bond [6].

Polyethylene terephthalate (PET) cords, which are belonging to the polyesters, are a much less reactive and an additional treatment is mandatory to obtain sufficient adhesion. The reason for this is the chemical inertness of the polyester which results in a poor compatibility to the RFL adhesive coating. Additionally, the solubility parameters do not match and therefore the thermodynamic compatibility is low: the solubility parameter (δ) of polyester is 10.3 $\text{MPa}^{1/2}$, while the RFL-dip has a solubility parameter of 16 $\text{MPa}^{1/2}$. A general rule says that a difference of more than 5 $\text{MPa}^{1/2}$ characterizes incompatible systems. To achieve adhesion between both components, an extra treatment of the cord is necessary to provide compatibility. Most common is an epoxy pre-treatment of the polyester cord. Thereby, a sub-coat is used which is situated between the cord and the actual RFL-coating. It is a water soluble or dispersible aliphatic poly-epoxy resin that contains aromatic groups. This sub-coat reacts with the polyester cord (Figure 5) and activates it for further interaction with the RFL-dip later on. The reaction is limited to the end groups of polyester polymer chains. Therefore, very high molecular weights will reduce the adhesion, as simply less end groups are available for the reaction with the epoxy dip. Oils and emulsifiers are used to overcome the hydrophobic surface effects of the cord to make it wettable for the poly-epoxy solution [6]. Furthermore, they disperse the epoxy groups properly during the treatment.

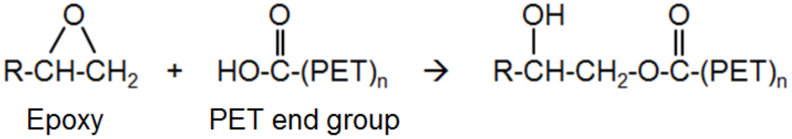


Figure 5: Schematic reaction pattern of an epoxy coating with a polyethylene terephthalate (PET) end group.

The epoxy coated polyester cord is expected to contain a number of unreacted epoxy groups on its surface. Those groups then will react with the resoles of the RFL coating which is subsequently applied in a second dipping step. With these two reaction steps, the epoxy coating can successfully bridge the incompatibility of both components and overcome the poor reactivity of polyester: Figure 6.

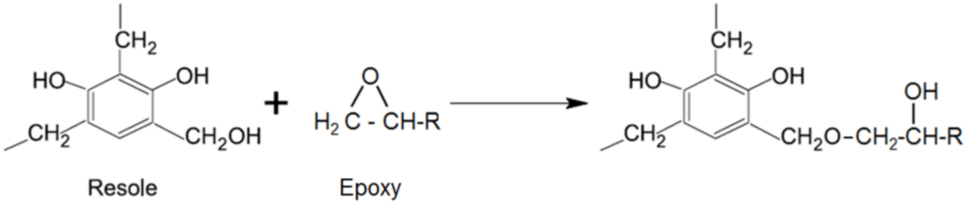


Figure 6: Actual reaction scheme of the RFL coating with the epoxy sub-coating.

Another approach for a pretreatment is the application of isocyanates. These groups can be used instead of epoxy and are able to form polyurethane groups which are much more compatible with the reactive moieties on the polyester surface from a thermodynamical point of view. They alter the polyester cord surface in a way that it is much more reactive towards the RFL-dip system.

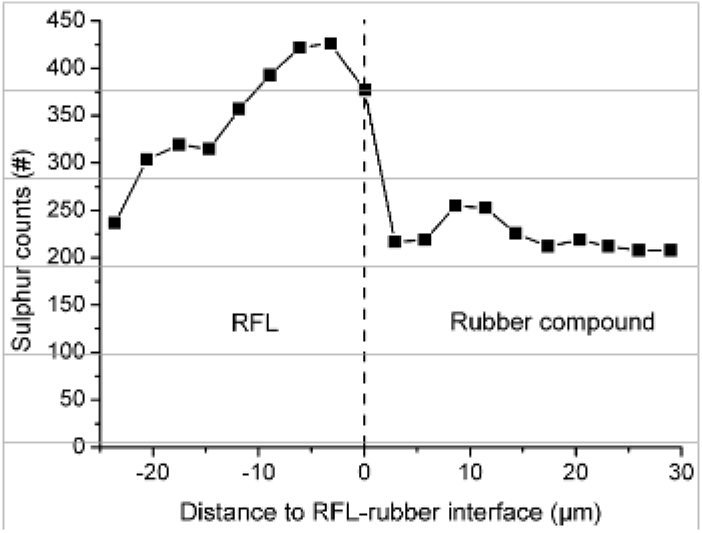


Figure 7: Plot of the sulphur counts over the distance of the RFL-rubber interface [4].

Next to the resin, also the latex component of the RFL-dip has to be cured in order to complete the adhesion. The heat treatment of the cord that is applied during the dipping process does not affect the latex phase, as the latex is missing a curing system that could start a cross-linking reaction. This fact is a good example of how well designed the RFL dip system is. During vulcanization, it takes advantage of the migration of sulphur complexes from the surrounding rubber compound into the latex phase of the RFL dip which causes also cross-linking of the latex. In Figure 7, the number of sulphur counts is plotted over the distance into the RFL-rubber interface. Clearly, the highest count can be found on the RFL-side which by origin does not contain any sulphur. This figure proofs, that indeed a migration of sulphur via diffusion is ongoing during vulcanization. The driving force for this effect is the significant difference of sulphur concentration between both sides and the given tendency of nature to balance concentrations equally. As the amount of sulphur found in the RFL after vulcanization is even higher than in the rubber phase, it can be expected that the cross-linking density is higher as well. This enhances the transition zone from the stiff cord to the highly elastic rubber even further.

Figure 8 shows the entire adhesion mechanism of a RFL-dip. On the left side is the cord and on the right side the rubber matrix. In between is the interpenetrating network of the RF resin and the latex. During the composite vulcanization, finally also the latex phase gets cross-linked, as described in the paragraph above. The two phases are not chemically bound to each other, but the interpenetration results in a strong bonding effect. As both are covalently bonded to one of the composites elements, the interpenetrating network allows the transition of forces that lead to the desired reinforcing effect. The key advantage of a RFL-adhesive is, that it features two components that can adhere very well to one of the composite materials, respectively. This is combined with an intimately interpenetrating network of both adhesive components.

In general, the RFL-dip systems deliver the best results for adhesion promotion between rubber und reinforcing cords. That is the major advantage of this technique, but it also has some drawbacks, and these are the driving forces to substitute the RFL-dip treatment with alternatives. The drawbacks are mainly the multistep processing, which is costly and requires time and effort, as well as the environmental burden and health aspects. Even though nowadays industrial setups provide high protection standards for workers and the environment, the residues from the RFL-dip processing often must be handled as special waste. The health concerns are mainly regarding evaporation of resorcinol during production and application of the dip. Resins that are containing higher levels of free resorcinol (> 5wt. %) are expected to exhaust toxic fume Resorcinol has a hazardous nature and is considered dangerous to the environment as well. Next to resorcinol, also formaldehyde is problematic, as it is highly toxic to all living beings, regardless of the method of intake, and is confirmed to be possibly carcinogenic (class 1B) [9]. Toxicologists expect that formaldehyde will be banned in the EU within the next 5 years.

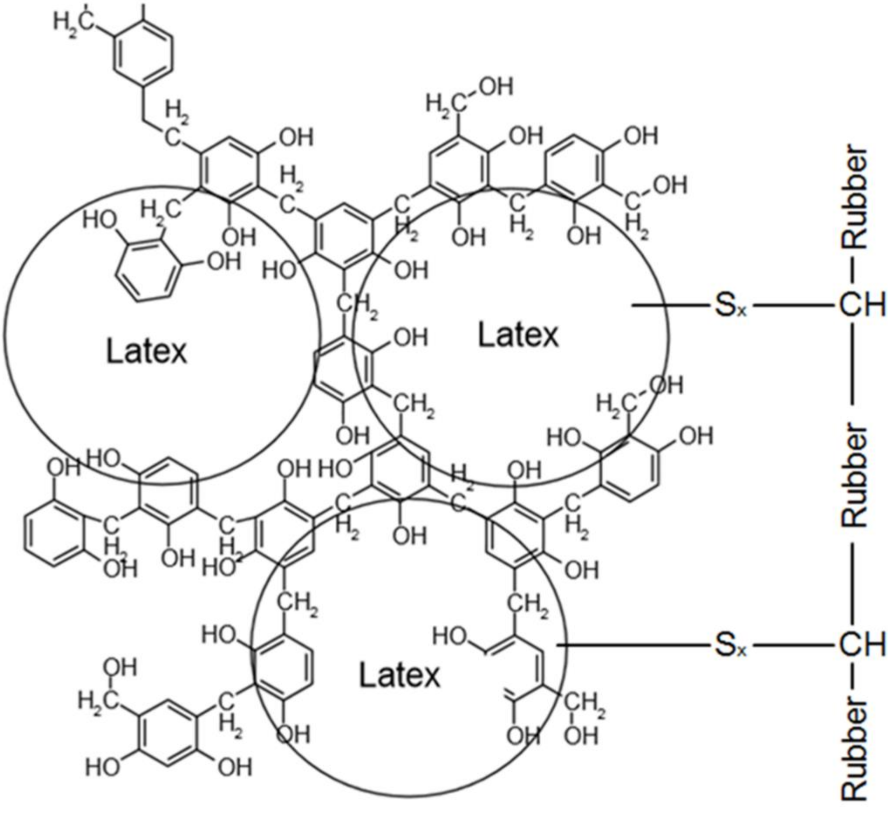


Figure 8: Overview on the adhesion mechanism of a RFL dip system [8].

From the aqueous processes, the main process wastes are the residues and washings arising at the end of the processing runs. These generally contain latex and resin, but are usually much less concentrated than normal dips. Such residues are sometimes accepted by the Water Authorities for treatment, provided that the pH, total solids and chemical oxygen demand fall within the limits of Consent to Discharge. Frequently, it is necessary to install pre-treatment systems to remove the bulk of solid materials. This then presents the problem of the disposal of the resultant solid matter, which again must be handled as special waste [7].

2.3 ALTERNATIVE ADHESION PROMOTION TECHNIQUES

If a prohibition of RFL or parts of its formulation within the next 5 years is likely, the question for alternatives is an urgent one. Next to the exceptional adhesion values, RFL is being used for all polymeric cords. Therefore, it is the industrial standard and the same chemistry is used by all tire manufacturers and producers of textile reinforcements all over the world. Another fact is, that it has proven to be a reliable adhesion system with respect to all circumstances in a tire life. A substitution of RFL is a substantial change for the entire tire industry. Therefore, a possible replacement should have the potential to become a comparable worldwide industrial standard.

The risk and hazard of formaldehyde is well known within the tire industry. A substitution of free formaldehyde with substances capable of releasing formaldehyde in-situ is a feasible alternative. The following chemicals can do so: trioxane (a $C_3H_6O_3$ ring), hexamine and melamine resins. However, they all share the necessity of either catalysts or higher temperatures to decompose those substances to release formaldehyde. This constraint makes it more attractive to the industry to find a replacement of formaldehyde than adding further reaction steps to the process that release formaldehyde in-situ. According to cord producers, a proper alternative need to meet the following conditions [10]:

- Multi-component system with good to excellent fiber-rubber adhesion
- Hazard-free storage, mixing and dipping conditions
- Applicability to the majority of:
    - Established polymeric cords
    - Established technical rubber compounds
- Hardening / cross-linking must be fast and reliable (ideally thermal)
- Stability at ambient temperature (several days)
- Aqueous solutions / suspensions preferred
- Low or tunable penetration depth into the fiber
- Intermediate modulus of adhesive layer (mechanical compatible)
- Adequate performance during the whole tire life at all conditions

According to (patent-)literature, several adhesive systems are described besides RFL. Clearly, the first logical option is to look for RF analogs like polyalcohol-polyaldehyde resins. Another promising option are (poly-)isocyanates, but also polyepoxides, polyphenylene ethers in combination with thermoplastic starch or polyfunctional silanes can be considered as potential alternatives to the RF resin.

However, these alternatives frequently have problems that hinder a replacement of RFL:

- Significantly higher costs
- Still usage of hazardous materials
- Solvent based dipping processes (instead of water based)
- 2- or more step dipping processes
- Inferior adhesion properties

From these facts, the conclusion can be drawn that the cord producers and the tire industry will continue to use formaldehyde and thus the complete RFL adhesion system in the future. Even though new thresholds will be introduced for the usage, a ban of formaldehyde is not expected within the next three years. The reasons that the industry prefers to further use RFL as long as possible are the good performance, the existing industrial production facilities and the low costs. Also, possible alternatives are most likely still hazardous and the risk is unknown. The constrains about the introduction of new adhesive systems are obvious, as the industry requests a joint approach of cord and tire producers to influence the authorities in the interest of prolonging the use of formaldehyde. An alternative – if necessary at all – should become a new industry standard [10].

This being said, the fact that it is very likely that the legislation of the EU will take action against formaldehyde creates the urgent need to look for suitable alternatives. In the following, the most promising candidates are introduced and their adhesion systems are explained and discussed in more detail.

2.3.1 Alternative impregnation techniques

Formaldehyde-resorcinol-free dipping systems are available for all polymeric cord materials including aramid. Ideally, the substituting chemicals have a lower risk, be less hazardous and are readily available on the market. It fulfills the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) regulation of the European Union from December 2006. There is a certain freedom to operate for many of these systems due to prior art in literature that prevents patent conflicts. Water based dipping processes are also described, which require hardly any additional adaption of existing dipping infrastructure. Adhesion and fatigue properties are reported to be equal or superior to RFL-dip, but these final conclusions still need to be confirmed in tire tests. A reasonable price/performance ratio compared to RFL can be expected [11]. However, this statement is in contrast to the conclusion drawn in the previous paragraph. Obviously, the will to accept the changes that are going to come within the industry is more and more established.

However, RF-free dips are also entering the market. A good example is the recent patent by Cevahir [12] of a RF-free dip which is in principle applicable to all reinforcing polymeric cords, but is only available for polyamide cord yet. The RF-resin is replaced by a composition made of acrylic resin (adjustment of the pH value required), epoxides, polyisocyanates and latex. That technique has the advantage of being an aqueous dipping solution too, which makes it possible to use similar processing steps and equipment. The dip pick-up is lower compared to RFL-dip at a similar adhesion level according to the supplier.

Another approach patented by Solomon [13] uses an acrylic resin too, which adds up on the conventional epoxy pre-dipping. It is suitable for polyester and aramid cords, that are dipped in a RF-free latex of a diene polymer in which an acrylic resin with a molecular weight in the range from about 100,000 to about 1,000,000 is dispersed. The acrylic resin is a copolymer consisting of two or more monomers, one of which is (meth)acrylic acid and another is a lower alkyl(meth)acrylic acid ester. This patent was filed back in 1983, which can be taken as an indicator that the development of alternatives is not a new trend.

2.3.2 Direct bonding of the cord to the rubber via cord backbone modifications

Bas [14] invented an entirely dip-free adhesion method. The principle is that the reinforcing cord has unsaturated bonds which can participate in the vulcanization reaction of the rubber matrix. In fact, there is no adhesive used at all. In theory, this is a perfect solution, as it significantly simplifies the whole adhesion process. The advantages are obvious: the entire dipping process that is commonly applied after twisting the cord is not needed anymore. That causes significantly lower production, processing and investment costs. Also, it is much more environmentally friendly, as it eliminates chemical treatments and improves the workers' health and safety.

The modification is done during the synthesis of the cord filaments. Unsaturated monomers are added at this process step. In case of polyamide, the synthesis comprises a polymerization reaction of diamines and dicarboxylic acids. The modification agent is added in the form of an unsaturated cyclic dicarboxylic acid. It participates in the polymerization and introduces unsaturated functional groups to the cord. The process is also suitable for polyesters, but here the dihydroxylic acids are modified to be unsaturated.

Figure 9 shows the reaction pattern. Like RFL, where the latex phase is cross-linked by the migrating sulfur, here the bonding between rubber and cord also requires sulfur from the rubber compound. According to the patent, the number of unsaturated double bonds is freely scalable. However, as much as this approach can simplify the production process of the cord, probably the efforts with respect to adhesion interface and tire construction are fundamental.

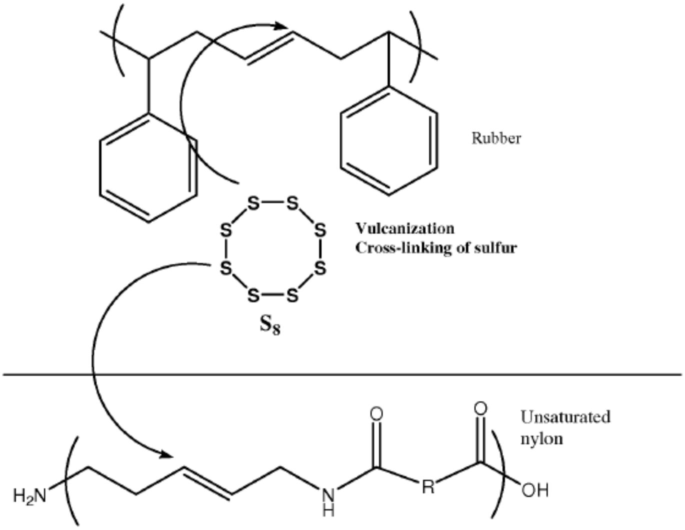


Figure 9: Reaction scheme of unsaturated polyamide and a rubber compound [14].

Such a polymer has the tendency of gelling because of the high number of double bonds and the use of inhibitors is required to avoid this. The heat treatment normally performed during the RFL dipping process is missing in this case, which affects the elongation and fatigue properties of a cord. The elongation of the unsaturated cords is higher, which can be compensated with the twisting of the cord.

2.3.3 Plasma technique

Plasma treatment is another competitive option for adhesion promotion. Plasma is basically an ionized gas, that contains radicals amongst other particles. These radicals make a plasma highly applicable for surface treatments, either to prepare a surface for an adhesive coating or creating an adhesive layer purely by plasma. The technique is available since the late 1950's. In the beginning the technology was limited to low pressure plasmas, which were realized in the industry as batch-wise processes. The development of highly sophisticated production systems where several treatment steps were automated and processed in-line, the need for atmospheric pressure plasma equipment lead to the development of a new generation of plasma generators. Since then, plasma equipment can be found in several industrial in-line production facilities, for example in the electronic industry. The main task is commonly surface cleaning and adhesion promotion. In the following paragraphs, the plasma technique will be explained in more detail and the possibilities to use it for the adhesion promotion between reinforcing polymeric cord and rubber will be analyzed.

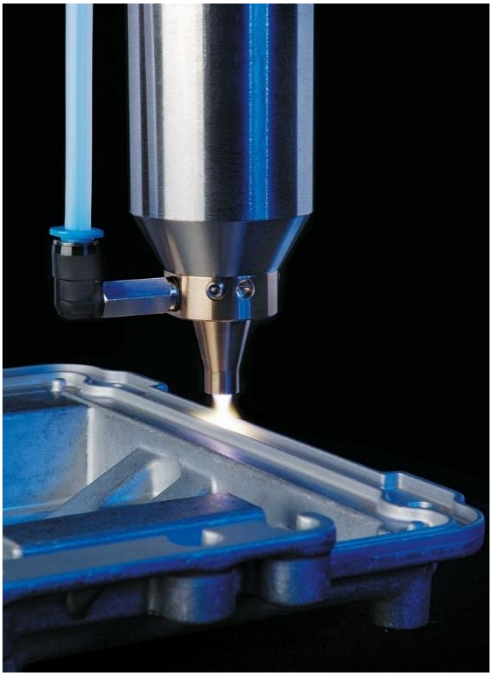


Figure 10: A plasma torch cleaning a metallic surface before application of an adhesive [15].

2.4 PLASMA GENERATION AND CLASSIFICATION

Plasma is generated by applying energy to a neutral gas. This high energy state causes ionization within the gas, as any volume of a neutral gas always contains a few electrons and ions [16]. These are present in the gas because of interactions of cosmic rays or radioactive radiation with the neutral gas. The additionally supplied energy causes that the free charge carriers are accelerated, and new charged particles might be created when these charged carriers collide with atoms and molecules in the gas. However, in its entity the plasma has an electrical quasi-neutral charge.

Plasma is defined as a state of matter, which is much higher energized than a solid, liquid or gas state. This definition was first suggested by Sir William Crookes in 1879, as he was naming the plasma state the ‘fourth state of matter’ [17]. These states are shown in Figure 11. However, the term ‘plasma’ was first used by Irving Langmuir in 1929. He denoted this state of a gas as plasma in an article about gases in electrical discharge tubes [18].

Ionization within a neutral gas can be established, when the gas molecules are subjected to electrical fields, high energy radiation or high caloric energy. The source for the energy can be a natural one or artificial by external excitation. The gas electrons are very responsive to this energy because of their insignificant mass compared to the relatively heavy particles. This excitation causes collisions of the neutral gas species with the gas electrons. These collisions [19] follow probabilistic laws and can be divided in:

- Elastic collisions: no change in the internal energy of the neutral gas species but a slight rise of their kinetic energy.
- Inelastic collisions: excitation is high enough that the electronic structure of the neutral gas species can be modified. Creation of excited species or ions if the collisions are energetic enough.

Consequently, plasma contains free charge carriers and is an electrically conductive as well as a chemically active media. The number of free electrons per unit volume is defined as the electron density and refers also to the term plasma density. The degree of ionization of a plasma is the proportion of atoms that have lost electrons due to excitation. The higher the energy level, the higher the rate of electron excitation and, therefore, the higher the degree of ionization.

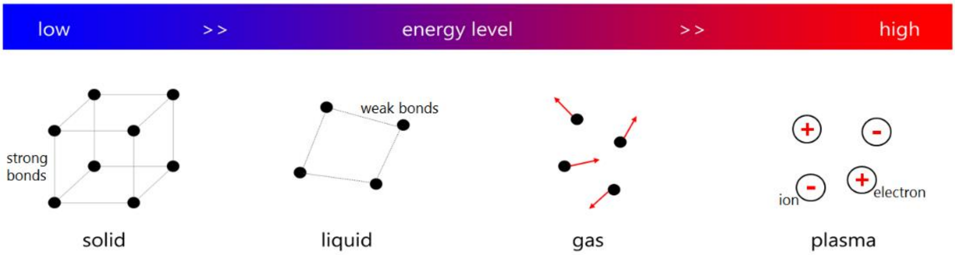


Figure 11: The four states of matter from the solid (left hand side) to the plasma state (right hand side). The drawing is based on [20].

There are two main categories for the classification of plasmas:

- Near-equilibrium plasma or thermal plasma,
- Non-equilibrium plasma or non-thermal plasma.

As the term thermal suggests, the equilibrium of a plasma is related to the temperature of the particles. In a near-equilibrium plasma, electrons and heavy particles (ions) have nearly the same temperature, and the temperature level is very high. Such plasmas are close to the maximum of ionization and have an extremely high energy content, which induces fragmentation of all organic molecules to atomic levels. A good example for this type of plasma is the sun (Figure 12), but most of these naturally existing plasmas in the universe have a rather low degree of ionization. Consequently, a thermal plasma can only be used in a few technical applications like the modification of thermally stable inorganic materials. In industrial scale it is barely used and applications are commonly not beyond laboratory or pilot scale stages.

Non-thermal plasmas contain mainly low temperature particles. In fact, they contain ions and neutral particles which have nearly room temperature, whereas the electrons have significantly higher temperatures. The degree of ionization is between 10^{-4} to 10 %, and therefore much lower in non-thermal plasmas than in thermal plasmas. An example is shown on the right-hand side of Figure 12, where a blizzard represents a natural occurring non-thermal plasma.

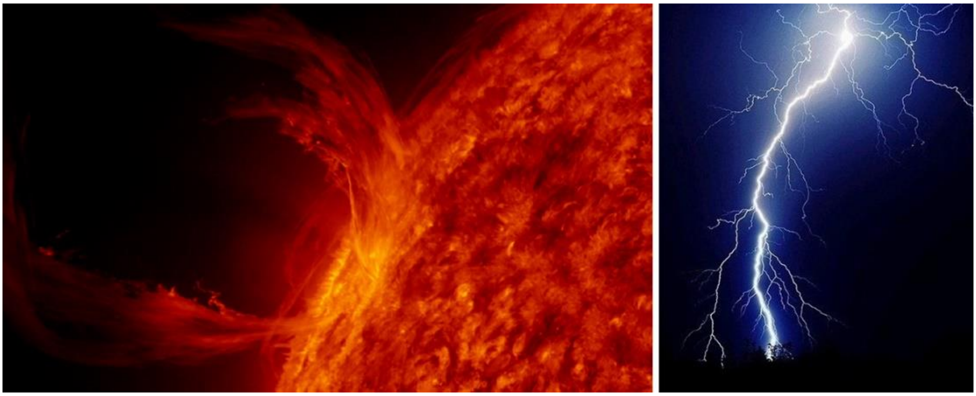


Figure 12: Examples for a thermal (left) and non-thermal (right) plasma.

Technically these plasmas are achieved by using an electrical field. Under low pressure conditions with less than 100 Pa, the mean free path distance of non-excited particles is too large for possible energy transfers. An external electrical field accelerates the responsive electrons selectively towards the anode. These electrons collide then with surrounding neutral gas particles and set further electrons free. This creates an avalanche of charged particles and a breakdown (discharge) of the gas takes place. If the discharge is balanced by charge carrier losses [16], a steady-state plasma can develop. Under normal atmospheric pressure such a discharge requires significantly more energy, as much more particles interact with the excited electrons. It is possible to gain a non-equilibrium plasma state with the help of dielectric electrodes and a high frequency alternating current. In every cycle, local discharges (streamer) at random places occur. Due to the high frequency, only the light electrons can follow the acceleration and can reach the anode, while the ions are too heavy and slow to react on the changing electrical field and, therefore, reach the cathode in time. The ion loaded gas stream then interacts with the surface of the substrate.

2.5 ATMOSPHERIC PRESSURE PLASMAS

Atmospheric pressure plasmas can as well be divided into these two categories which were introduced in the former paragraph. The thermal plasma is called local thermodynamic equilibrium (LTE) plasma and the non-thermal (cold) plasma is called non-local thermodynamic equilibrium (Non-LTE) plasma. It is important to distinguish between both, as several plasma parameters (for example particle distribution functions and electron, excitation, and vibration temperatures) are depending on the type of atmospheric pressure plasma [19].

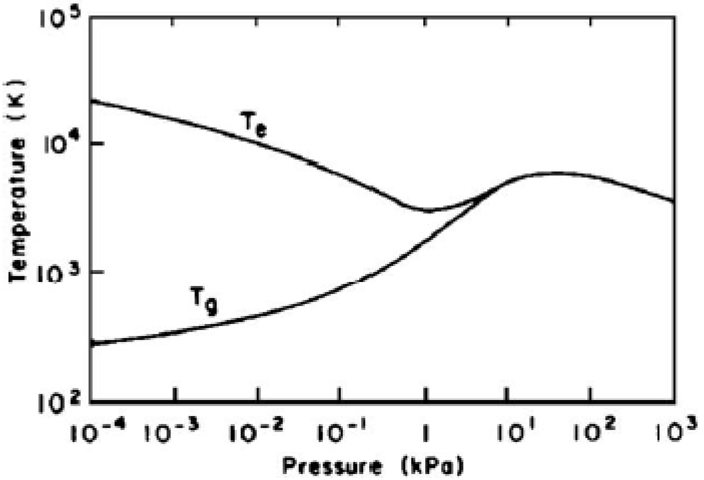


Figure 13: Development of plasma particle temperature over pressure [21].

The difference between both plasma types can be seen in Figure 13. In the low pressure range from 10^{-3} to 10^{-1} kPa, a significant gap between the electron temperature (T_e) and the gas temperature (T_g) is observed, which represents the neutral and heavily charged particles. An increase of pressure causes a reduction of the temperature gap between electrons and heavily charged particles. This explains why the plasma type changes with increasing pressure from non-LTE to LTE. This transition can also be described as a change from glow discharge (non-LTE) to arc discharge (LTE) [22]. Inelastic collisions between excited electrons and heavy particles are determining the plasma properties in the low-pressure range. With increasing pressure, the number of elastic collisions also rises. The elastic collisions lead to an increase of T_g and thus the temperature gap between electrons and heavy particles decreases. Therefore, the plasma is getting closer to a thermodynamic equilibrium stage. The higher the deviation from LTE, the more significant the gap between T_e and T_g is.

2.5.1 LTE plasma

In case of a LTE plasma, transitions and chemical reactions are initiated by inelastic or elastic collisions, but not by radiative processes. Furthermore, these collision phenomena must be micro-reversible. As a matter of fact, each kind of possible collision must be balanced (excitation/de-excitation; ionization/recombination; kinetic balance) [23] within the plasma.

Moreover, local gradients of the plasma properties must be low enough in order to allow particles reach to an equilibrium state in the plasma. And the diffusion time, which is the time the plasma must diffuse before recombination, must be sufficiently long to allow the particles to reach an equilibrium in the plasma [21].

2.5.2 Non-LTE plasma

With the departure from the Boltzmann distribution – which is an indicator of the probability that a system is in a thermodynamic equilibrium state at a fixed temperature – for the density of excited atoms within the plasma, the deviation from the LTE conditions can be explained [19]. The reason for this is, that for low energetic levels, the electron induced de-excitation rate of gas atoms is in general lower than the corresponding electron-induced excitation rate, caused by a significant radiative de-excitation rate [23].

Table 6: Main characteristics of LTE and non-LTE plasma [19].

	LTE plasmas	**Non-LTE plasmas**
Current name	Thermal plasma	Cold plasma
Properties	$T_e = T_g$ High electron density: 10^{21}–10^{26} m^{-3} Inelastic collisions between electrons and heavy particles create the plasma reactive species, whereas elastic collisions heat the heavy particles (the electrons energy is thus consumed).	$T_e \gg T_g$ Lower electron density: $<10^{19}$ m^{-3} Inelastic collisions between electrons and heavy particles induce the plasma chemistry. Heavy particles are slightly heated by a few elastic collisions (that is why the electrons energy remains very high).
Examples	Arc plasma (core) $T_e = T_g$ = 10.000 K	Glow discharges T_e = 10.000 – 100.000 K T_g = 300 – 1000 K

The mass difference between electrons and heavy particles is also a factor for the deviation from the LTE state. Electrons are highly mobile, while heavy particles are quasi static in the plasma. The higher the temperature difference between the particles, the more problematic the formation of an equilibrium state will be. Often partial LTE (pLTE) plasmas are formed, where the LTE distribution is only partially present close to the ionization zone [24].

2.6 GENERAL INDUSTRIAL PLASMA PROPERTIES

Before different plasma reactor types will be explained, first a look at some characteristics of plasma, which are important in industrial applications, will be taken. Commonly, all industrial realized plasma solutions are Lorentzian plasmas, which are plasmas where collisions of excited electrons with neutral background gases are predominant [25]. The mobility of species within a plasma is a function of the collision frequency. It is roughly constant for a given pressure of the neutral gas background. This is of interest, as the drift velocity of a species can be described with its help as being directly proportional to the electric field which is applied to the plasma. Moreover, the electron collision frequency plays a significant role in describing power dissipation in plasma and in all transport coefficients used to determine plasma properties.

Photon emissions caused by excitation collisions are responsible for the visibility (glow discharge) of plasma. However, the electron energy is also converted into heat by the inelastic collisions with neutral particles. This effect is called ohmic heating of plasmas, which yields to a plasma value called power density. In case of solid materials, the terms electrical conductivity σ and electrical resistivity ρ are constant properties, as they are valid at any position within such a material. In plasma this is different, as σ and ρ are usually functions of the position in a plasma [25]. Therefore, the usability of these values is in case of plasma very limited. The energy transfer frequency is introduced to overcome these shortcomings and is defined as the frequency with which the electrostatic energy density provided by external power supplies is transferred to the plasma.

The fact, that a plasma is on macroscopic level a quasi-neutral media, was already mentioned and is a direct consequence of the presence of oppositely charged species which create strong electrical forces [25]. To maintain the separation of these species in a plasma, externally imposed electrical fields or enough thermal energy of the plasma itself are required. The former is commonly the case for industrial plasmas. These circumstances are handy for calculations, as any industrial plasma will contain almost exactly the same number of positively and negatively charged species, which makes it unnecessary to consider the ion or electron density population separately.

In a polarized plasma, a separation of electrons and heavy, positive ions is established. During the off-time of the applied electric field, the much lighter electrons are highly attracted by the nearly immobile ions. The electrons will oscillate amongst the ions, but that oscillation is dampened by collisions. The frequency of these collisions is expressed with the electron plasma frequency [25]. In case of industrial plasmas with a characteristic number density of about 10^{16} particles/m^3, the electron plasma frequency is 0,9 GHz. This frequency is critical when it comes to propagation of electromagnetic radiation. Depending on the wavelength of the electromagnetic radiation and the plasma frequency, the radiation might be mostly reflected or transmitted.

2.7 PLASMA POWER SUPPLIES

To generate an industrial plasma, the following three types of current for power supplies are available:

- Direct current (DC),
- Alternating current (AC),
- Radio frequency (RF).

As the technology developed later in the present thesis is based on RF, the focus in this paragraph is on that plasma power supply type. RF is also the most expensive type, because it cannot be connected directly to the plasma reactor, like it is the case for DC and AC power supplies. The whole build-up of a RF power supply is much more complex. The extra effort of this power supply can only be justified by operational advantages. And indeed, a RF driven plasma reactor gives a greater stability during operation. Moreover, it provides a higher electron kinetic temperature, which is beneficial in cases where a high number of free radicals in the plasma is necessary to enhance the chemical reactivity of the plasma. Also, RF reactors do have a better electrical efficiency that reduces the operation costs. The industrial power level of these reactors is in the region of 200 W to 50 kW (see Figure 14), even though there are applications that require generators in the range of 1 MW. RF power is about 5 to 10 times more expensive as DC power according to a rough estimation done by Roth [25].

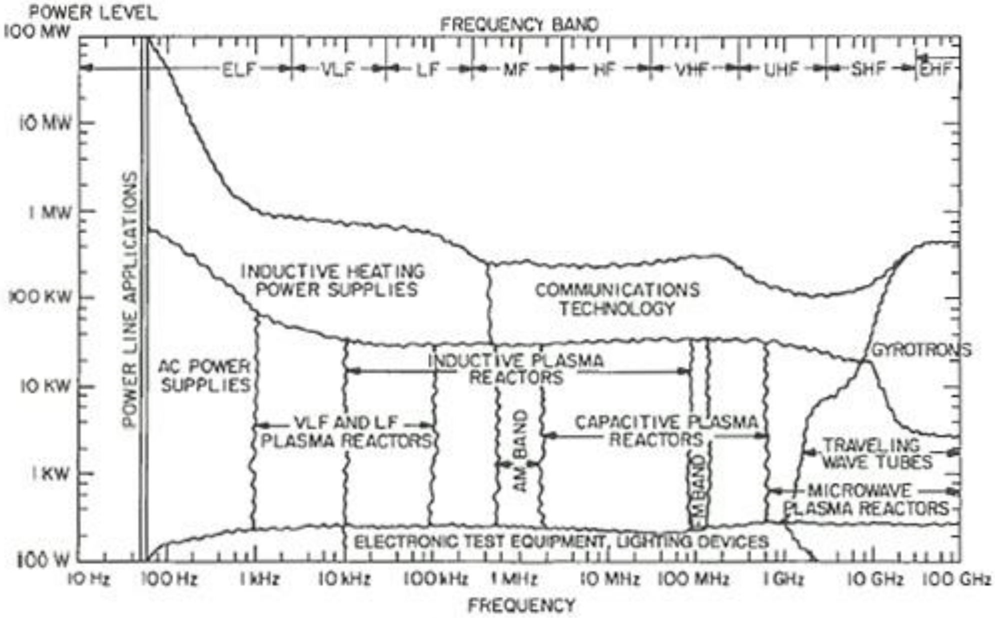


Figure 14: Availability of radio frequency power [25].

Certain frequencies are reserved for industrial high-power supply, so that most RF power supplies work at similar frequencies. Some of these frequencies are 400 kHz, 450 kHz, 3.0 MHz, 13.56 MHz, 27.12 MHz, 0.915 GHz and 2.45 GHz [25], where 13.56 MHz is a very common RF frequency for plasma reactors. Besides those restrictions in frequencies, also safety related operating regulations in case of high power RF plasma generation do apply [25]:

- *RF arcs:* can strike and be maintained over great distances, in particular at low frequencies.
- *High voltage RF shielding:* RF plasma reactors are able to function similar to a radio antenna. It is possible that they induce high voltages on electrical conductors that are located nearby.
- *Frequency drifts:* Shielding to avoid interferences with other devices using the electromagnetic spectrum at different frequencies than the assigned one.

2.8 INDUSTRIAL PLASMA TYPES

2.8.1 Corona discharge

Corona discharge is a non-LTE discharge with low current density. The device consists of a cathode-wire and an anode (the treated material), and the DC power supply is pulsed. When a high voltage is applied across the electrodes, a plasma is formed and a light blue color can be observed in the air gap between the electrodes. The insulating covering of the grounded roll prevents a direct arc between the two electrodes. The plasma creates a lighting crown around the wire: that is why this discharge is called ‘‘Corona’’ [26]. This technique is one of the first plasmas that have been used industrially and is still widely used in surface modification of polymers for printing and adhesion applications. Often a corona discharge plasma is used for continuous treatment of films, installed downstream of an extruder. Similar to a flame treatment, a corona treatment causes surface oxidation of polymers. Electrons, ions, excited species and photons that are present in a discharge react with the polymer surface to form radicals. These radicals react rapidly with atmospheric oxygen.

The restricted area of the corona discharge has limited its applications in materials processing. To overcome this problem, two-dimensional arrays of electrodes have been developed. Some applications of coronas include the activation of polymer surfaces, and the enhancement of SiO_2 growth during the thermal oxidation of silicon wafers [26].

A corona discharge ignites its plasma at a voltage of 2–5 kV and produces an extremely small current of 10^{-10} - 10^{-5} A. Above 10^{-5} A, the voltage rapidly increases with current. This coincides with the generation of micro-arcs that extend between the electrodes. A maximum voltage is reported at a current of about 5×10^{-4} A. At this voltage, the device begins to arc. Therefore, corona discharges are operated at currents below the onset of arcing [26].

In the plasma near the tip, the density of charged species rapidly decreases with distance from about 10^{13}-10^{9} cm^{-3}. The electron temperature within the plasma averages at about 5 eV. In the drift region outside the discharge, the electron density is much lower, near 10^{6} cm^{-3} [26].

Advantages of corona and flame treatments are that these processes can be used in continuous operation, and that the required equipment is very simple and cost effective. The disadvantages arise from the fact that both treatments are carried out in open air, which often makes it difficult to control the uniformity or chemical nature of the modification, due to variations in ambient conditions such as temperature and humidity or contaminations. Characteristic for corona discharges are an asymmetric electrode pair, as they are used in form of a point or wire cathode and a planar anode in various setups.

A highly non-uniform electric field is created using a continuous or pulsed direct current (DC) voltage. Near the point electrode, the potential gradient of the electric field is high enough to form a conductive region, but not high enough to cause a breakdown of the gas. This enables a weakly ionized local plasma, which is spreading out through the drift region to the planar electrode. This phenomenon of local discharge is called corona discharge. It can appear in several forms, depending on the polarity of the field and the geometrical configuration of the electrodes. A corona discharge is a progress of multiple sequential steps, starting with free electric charge available from the applied high voltage. It builds up an avalanche that enables an excess electric charge continuum to be distributed over a region of space around the cathode. Photons from the avalanche create new charge carriers outside that region and closer to the cathode than the former one. A continuous process of these steps then enables a corona discharge [27].

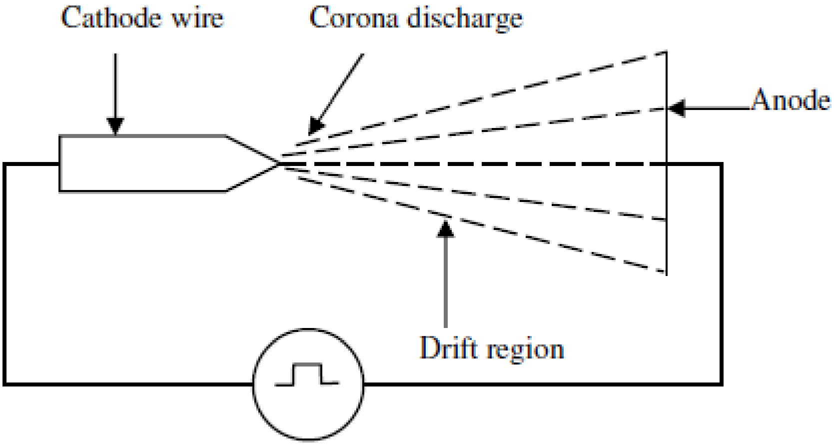


Figure 15: Common schematic setup of a corona discharge [27].

According to the polarity of the electrode, formation of positive or negative ions takes place. If the electrode is positive, a positive corona is created and vice versa for a negative electrode. The physics of positive and negative coronas are significantly different. This asymmetry is a consequence of the vast difference in mass between electrons and positively charged ions. Only the light weight electrons have the ability to create a significant degree of ionization due to inelastic collision at common temperatures and pressures [28].

Applications for corona discharges in the industry are mainly electrostatic precipitators (ESP), which are usually used to collect dust in industrial off gases. Furthermore, this plasma technique is used in water purification, electrophotography, printers and powder coating. For material processing, the inherent non-uniformity of corona discharges limits the possible applications of it in this field.

2.8.2 Dielectric barrier discharge

A frequently used atmospheric plasma source is the dielectric barrier discharge (DBD), which was invented by Siemens in 1857 for the generation of ozone [28]. It consists of two metal electrodes, where at least one of them is coated with a dielectric layer (e.g. glass, quartz, ceramic). The dielectric serves two key functions in the discharge operation [29]: (i) it limits the amount of charge transported from one electrode surface to another via a single micro-discharge and (ii) it distributes these micro-discharges over the entire electrode area. Usually, voltages of a few kV and frequencies ranging from 5 to 500 kHz are used. To ensure stable plasma operation, the gap which separates the electrodes is limited to a few millimeters wide. Plasma gas flows in the gap. The discharge is ignited by means of a sinusoidal or pulsed power source [19]. Depending on the working gas composition, the voltage and frequency excitation, the discharge can be either filamentary or glow. A filamentary discharge is formed by micro-discharges or streamers that develop statistically on the dielectric layer surface. The electrons accelerated under atmospheric pressure conditions undergo a very high number of inelastic collisions with gas particles. Besides the very fast excitation process (about 10 picoseconds), the de-excitation and recombination process also are rapid ones (about 100 microseconds). Consequently, this time frame is not sufficient for a removal of active species from the discharge zone by diffusion. Thus, the gas phase is mediated by free-radicals and surface reactions will be initiated and sustained by them. The mean electron energy in DBD plasma is in the range of 0–10 eV, while the chemical binding energy of polymers is less than 10 eV. Therefore, energetic particles in DBD can break the chemical bonds of polymers. In addition, modification of the surface properties of polymers without an expensive vacuum system is another advantage of DBD [29]. Due to the dielectric layer, the electrodes are separated from the discharge. Therefore, it protects them against etching and corrosion effects. Besides a plane-parallel DBD electrodes arrangement (volume discharge, Figure 16), also cylindrical or coplanar (surface discharge) arrangements are possible.

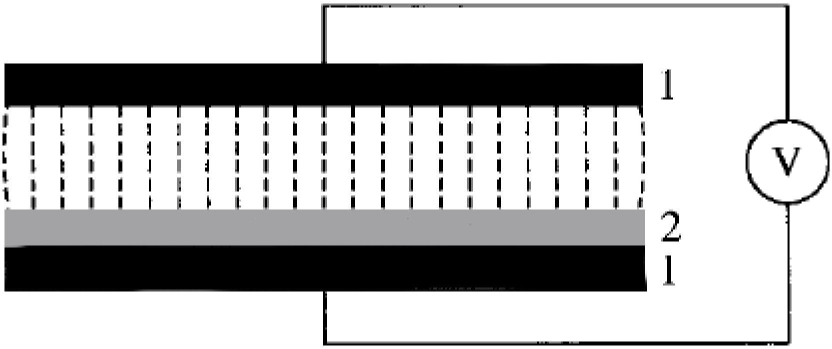


Figure 16: Schematic of dielectric barrier discharge; (1) electrodes and (2) dielectric barrier coating [26].

Dielectric barrier discharges are also called “silent” and “atmospheric-pressure-glow” discharges [26]. DBD plasmas are sometimes confused with coronas, because the latter sources may also exhibit micro-arcing. Several material processes have been examined for DBD plasma, including the cleaning of metal surfaces and the plasma-assisted chemical vapor deposition of polymers and glass films. However, since the plasma is not uniform, its use in etching and deposition is limited to cases where the surface does not need to be smooth. For example, in the study of SiO_2 deposition, it was found that the surface roughness exceeded 10% of the film thickness [26].

Initially DBD plasmas were developed and used to generate ozone for the treatment of drinking water. With the introduction of more and more polymeric materials in the industry, there was a demanding interest in surface treatments of these plastics, as their original surface properties were not optimal for bonding, printing, coating and adhesion applications. To overcome these shortcomings, it was necessary to modify the rather low surface energy of polymers [30]. Initially, corona discharge treatments under atmospheric conditions were used to modify polymer foils at production speed. Nowadays these devices are far more developed and are in fact DBD installations. A significant advantage of DBD plasmas is, that the dielectric element prevents sparks and, therefore, electric puncture of plastic goods. Also, electrically conductive and metallic foils can be treated [30]. Since the introduction of microcomputer-controlled power supplies in the generator technique, more sophisticated generator types for DBD plasma generation were developed. Their main ability is to respond automatically to the resonance frequency and adjusting the operating frequency accordingly. Another development are generators which are able to generate repetitive pulse trains instead of continuous sinusoidal voltage wave forms. The advantage of that technique is a more uniform distribution of micro-discharges and an improved surface treatment [31].

Like a treatment with a low-pressure oxygen plasma, the atmospheric pressure DBD plasma treatment produces a significant gain in surface energy. In case of plastic foils, the surface energy increases from 20-30 mJ/m^2 in the untreated case to 50-70 mJ/m^2 after the DBD plasma treatment [30]. This gain in surface energy is very useful for adhesion and print applications, as it enhances the wettability of the polymer.

A more recent development are glow-discharges controlled by a dielectric layer at atmospheric pressure. These stationary transient discharges are characterized by a periodic discharge current and have the same structure as that observed for a low-pressure discharge. The atmospheric pressure glow discharge (APGD) behavior can be described from the initiation to the extinction of the discharge [32]: the breakdown is obtained under uniform field, no constriction is observed. As the ion density increases, a cathode fall is created. Its thickness becomes smaller and smaller until the maximum of current is reached. This decrease in the cathode fall length allows one to self-sustain the discharge even if the gas voltage is divided by a factor of 2. The maximum values of electron and ion densities are about 10^{11} cm^3. After the current maximum, the thickness of the cathode fall increases slowly and the positive column length decreases. When the gas voltage polarity changes between two consecutive discharges, a residual electronic current is observed. This current is a memory of the positive column and an indication that the number of electrons in the gap will be sufficient to produce the next breakdown under a low field, which is a necessary condition to obtain an APGD. A density of electrons higher than 10^6 cm^3 at the breakdown voltage seems to be necessary to obtain an APGD controlled by a dielectric layer.

Recent investigations on low-current-density diffuse dielectric-barrier discharges also suggest novel applications of mild plasmas for sterilization and disinfection purposes and for selectively influencing biological cells [30]. If reliable control of these diffuse discharges can be obtained in an industrial environment, further applications of dielectric-barrier discharges for surface modification are to be expected.

2.8.3 Atmospheric-pressure plasma jet

An atmospheric pressure plasma jet (APPJ) consists of two concentric electrodes, between these electrodes a gas stream is flowing, see Figure 17. The streaming gas is usually air, nitrogen, helium, oxygen or another suitable gas, also mixtures of these gases are possible. Commonly the inner electrode is coupled to a 13.56 MHz RF power at a voltage between 100–250 V [26], while the outer one is grounded. The gas discharge is ignited through applying power to the inner electrode and operates on feedstock gas. The ionized gas exits the plasma jet through a nozzle, which results in a high velocity (about 12 m/s) stream of highly reactive chemical species at an effluent temperature of usually below 150˚C.

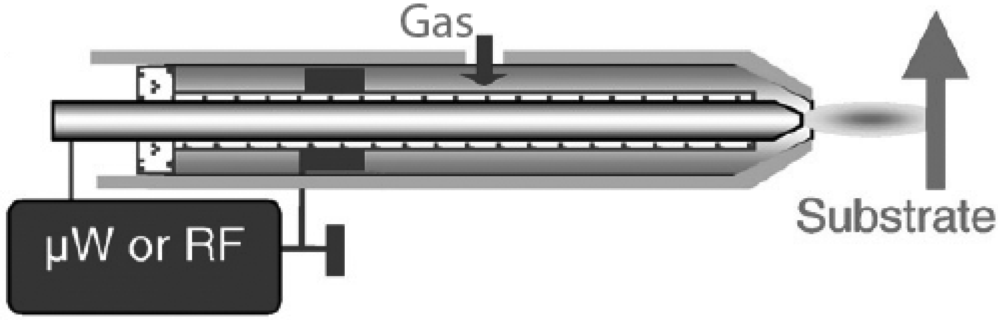


Figure 17: Coaxial RF atmospheric pressure plasma jet scheme[33].

The inner electrode accelerates free electrons, which undergo inelastic collisions with the processing gas. These collisions provoke excitation of molecules and atoms which form free radicals and additional ion-electron pairs. After passing the nozzle, a rapid recombination of electrons and ions occurs, but the effluent gas stream still contains neutral metastable species and radicals [26, 27]. The technique prevents arcing and produces a stable, homogenous and uniform discharge and lowers the gas temperature, which can be as low as 50˚C. In general, it can be said that APPJ technology exhibits great similarity to vacuum DC glow discharge plasmas.

APPJs have recently gained much interest [34]. They offer chamber-less delivery of downstream reaction chemistry, ideal for polymeric surface modification [35, 36], bacterial and biomolecule inactivation [37, 38], wound healing [39] and nano-structure fabrication [40, 41]. A distinct characteristic of a plasma jet configuration is its ability to generate a stable discharge in an inert gas atmosphere and then to transport the plasma to a separate region of reactive gas for processing applications, thus providing chemical reactivity without compromising plasma stability [42]. This spatial separation of the plasma generation and surface processing regions enables a considerable flexibility in jet designs to vary and control both, plasma dynamics and reaction chemistry [34]. Atmospheric plasma jets can be generated in many different gases and using different electrical excitations.

Depending on jet configuration and electrical excitation, plasma characteristics may differ significantly [34]. Typically, DC and microwave jets produce hot dense plasmas and are ideal for treating heat resistive materials. For heat-sensitive materials, the gas temperature needs to be reduced drastically. This can be achieved by placing the sample far away from the jet nozzle, employing fast gas flow, generating small plasma volumes and/or using different excitation frequencies. RF plasma sources have lower gas temperature and good plasma stability benefitting partly from electron trapping and from efficient electron heating at the sheath edges [43, 44]. However, for treating heat-sensitive materials, it is still desirable to reduce the gas temperature particularly at high RF power. This may be addressed by using pulse-modulated RF excitation [45, 46]. At lower frequencies below 100 kHz, sub-microsecond pulsed excitation is found to effectively reduce gas temperature [18, 42, 47-51]. In principle, it is possible to use nanosecond pulses and produce room-temperature atmospheric air plasma even at the core of the discharge [51].

An advantage of the APPJ design is the fact, that it is relatively easy to inject additional substances into the plasma stream. This is useful for coating applications. In Figure 18 such a construction is shown. The plasma is ignited between the electrode and the isolated housing inside the jet. Due to the gas stream that is ensuing from the gas supply towards the nozzle head, the plasma is carried to the substrate. The nozzle head features the possibility to inject a precursor, which can be any vaporizable substance, into the plasma. The plasma partly atomizes the precursor, which quickly recombines and further reacts on the substrates surface with surrounding elements.

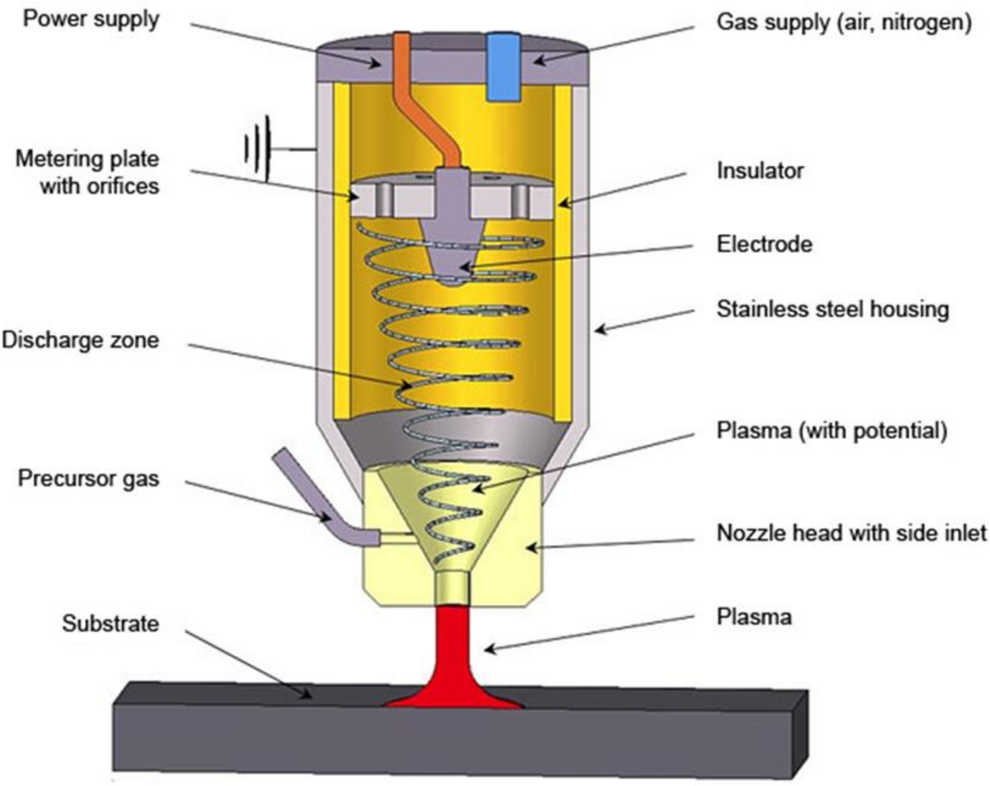


Figure 18: Construction of an APPJ with the ability to inject a precursor gas [15].

A prediction of the reaction pattern is not possible. This phenomenon causes an uncontrolled polymerization when monomers are used as precursor, in fact there is no repeating unit detectable. However, statistically the plasma polymerized polymer can be characterized. It is not feasible to form a polymer that features a high degree of steady configuration and a close distribution of its molar mass. This type of APPJ plasma unit will be used in the present work to deposit an adhesive layer on the polymeric cord to promote adhesion.

2.9 STATE OF THE ART

2.9.1 Patent situation

The idea of plasma treatment to enhance the adhesion between rubber and polymeric reinforcement cords is not entirely new. The aim was initially to enhance the adhesion of the standard RFL methods by plasma treatment. One of the first patents filed in this field belongs to Lawton et al. [52] and dates back to 1974. The topic is “Bonding of Poly(Ethylene Terephthalate) Induced by Low-Temperature Plasmas” and claimed is a low pressure plasma reactor which batchwise treats polyester in a non-oxidizing plasma. Sharma et al claimed a similar patent for the adhesion of aramid cords to rubber in 1984 [53]. An aramid cord is treated with plasma of air, N_2, He, Ne or Ar or a mixture thereof. It was found, that the adhesion for a dipped cord could be increased by up to 50 %. For un-dipped cords the adhesion was improved by up to 30 %. This patent does not state clearly, if it is an in-line atmospheric pressure or a batchwise vacuum process. The same inventor claimed in 1987 another patent, where the aramid cord was treated in the same way before dipping in a vinyl pyridine latex solution [54]. Furukawa et al. invented in 1988 an ion plating process in combination with the presence of polyamide vapor under reduced pressure [55]. The ion-plated material with a polyamide deposition was afterwards impregnated with an RFL adhesive.

The Goodyear Tire & Rubber Company claimed several patents in this field starting from the 1990’s up to the present day. As they show the development of their efforts on plasma treatment, these patents will be discussed in more detail. In a patent [56] filed by Shuttleworth with the topic “Process for the Surface Treatment of Polymers for Reinforcement-to-Rubber Adhesion” from 1991, a gas plasma of O_2 and tetrafluoromethane (CF_4) was used to activate the surface and make it more receptive to adhesives. Basically, that treatment is a cleaning step, as it removes hydroxy groups and other weakly bonded species such as sulfates, carbonates, low molecular weight polymer as well as processing aids. The treated cord was then exposed to an RFL adhesive. The plasma type is not specified, only a pressure of 0.001 to 1 torr (760 torr = 1 atm) and a plasma generation with a frequency ranging from about 50 Hz to 2.45 GHz was given. Such a treatment reached a level of 40 % of the strength compared to a conventional epoxy/RFL adhesive. Furthermore, they propagate another invention, where a polymerizing gas is introduced into the plasma chamber. Gases like sulfides, thiols, or isocyanates are polymerized on the cord surface and contain functional groups that can react with the elastomer matrix during curing. It was reported, that the latter treatment method results in a good adhesion. Later on this patent was extended with a new patent [57], where carbon disulfide (CS_2) was used as polymerizing gas. It is to mention, that the plasma treatment in this work took several minutes. Another approach was claimed by Parker in a further patent [58] from 1996, where reactive groups containing active hydrogen were bonded to a polymeric cord surface. As processing gas NH_3 and mixtures of CF_4/O_2 were used. It was expected, that these active hydrogen groups can react later on with blocked isocyanates at elevated temperatures, and form a chemical bonding to the elastomeric rubber network. For this patent, a power range from 50 to 5000 watts was claimed.

Further efforts of Goodyear were discussed in another patent [59] with the title “Vinyl Compound Plasma Pre-Treatment for Promoting the Adhesion Between Textiles and Rubber Compounds” patented in the year 2000. They analyze the use of CS_2 as plasma gas to deposit a sulfur-containing film on the cord surface and consider this method as ineffective, because the rubber latex particles in the RFL are hindered by the resin component and therefore they are less reactive towards the sulfur surface layer. Instead of this method, they propose the introduction of vinyl-groups on the cord surface followed by a RFL-treatment. Alternatively, to the O_2/CF_4 cleaning step, an ammonia plasma pre-treatment is suggested, which removes the unwanted debris and impurities from the cord surface, but additionally adds carboxyl- or amino-linkages. These functional groups can react with the vinyl groups generated from such a plasma. The plasma treatment used in this patent is based on a low-pressure environment and a power range of 5 W to 2.5 kW with treatment times between 5 seconds and 5 minutes. The type of plasma generation is not specified. Several different vinyl-containing plasma gases have been used, for example acrylic acid, ethylene, butadiene and vinyl pyridine.

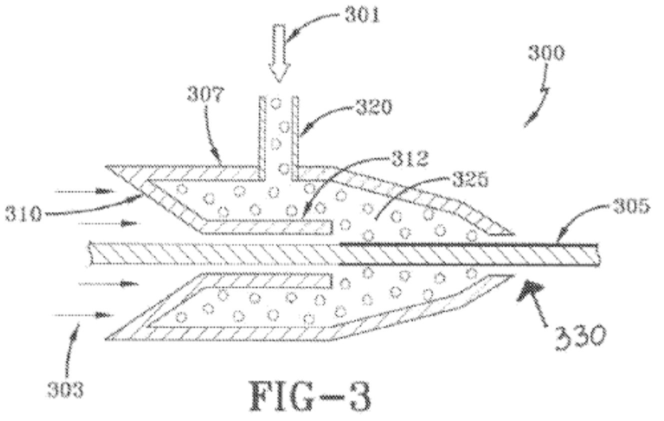


Figure 19: Drawing of a plasma polymerization nozzle from the Goodyear Tire & Rubber Company [60].

More recently new patent applications were claimed by the Goodyear Tire & Rubber Company, where one is about a plasma polymerization nozzle for depositing polymeric material on a reinforcing cord, while the other patents are about a method where an atmospheric plasma is used to treat reinforcement cords for rubber articles. The patents claim a method for steel and polymeric cords. The plasma polymerization nozzle [60] (see Figure 19) comprises an inlet (310) for receiving both, the cord and the plasma (303), coaxial to the outer body. Another radial inlet (320) on the top is available to receive a precursor material (301). Inside the nozzle is a mixing chamber (325) where the plasma activated cord gets in touch with the precursor, which can deposit on the surface of the cord and then exits the mixing chamber through another coaxial nozzle (330). The potential advantage of such a construction is, that the plasma activated cord is protected by the plasma gas until it gets directly in contact with the precursor material. This eliminates potential disturbances from the environment and thus prevents unwanted reactions. Such a nozzle is also very applicable for in-line processing of reinforcing cords in large quantities.

Another plasma treatment method seems to be the Goodyear's most recently published work in this research field and is valid for steel and polymeric cords. The US patent application from 2011 is filed by Siffer and is named "Atmospheric Plasma Treatment of Reinforcement Cords and use in Rubber Articles" [61], a similar European patent application [62] is also available. The method comprises mainly three steps:

a) atomizing a mixture of at least one polymerizable monomer, a halogenated saturated hydrocarbon, an optional curative and a carrier gas to form an atomized mixture;
b) generating an atmospheric pressure plasma from the atomized mixture;
c) exposing the reinforcement cord to the atmospheric pressure plasma under conditions suitable to form a polymer strongly bonded to the tire cord and capable of bonding to rubber.

The application claims several chemicals that are used to create an atomized mixture. As possible carrier gases are named argon, helium, neon, xenon, oxygen, nitrogen and carbon dioxide. From this choice, it can be anticipated that a non-reactive inert gas is regarded as most suitable for this method. As polymerizable monomers are listed isoprene, butadiene, squalene and styrene. Furthermore, several halogenated saturated hydrocarbons are listed. Specific sulfur containing compounds are not claimed in the patent applications. Also, not specified is the type of plasma generator for that method, in the claims is a dielectric barrier discharge listed, but in the general description all possible plasma types are named. In this method, the plasma treated cord will be wound on a spool, so a direct coupling with rubber is not planned. Even though it is not stated clearly in the patent application, this method is suitable for an in-line processing arrangement.

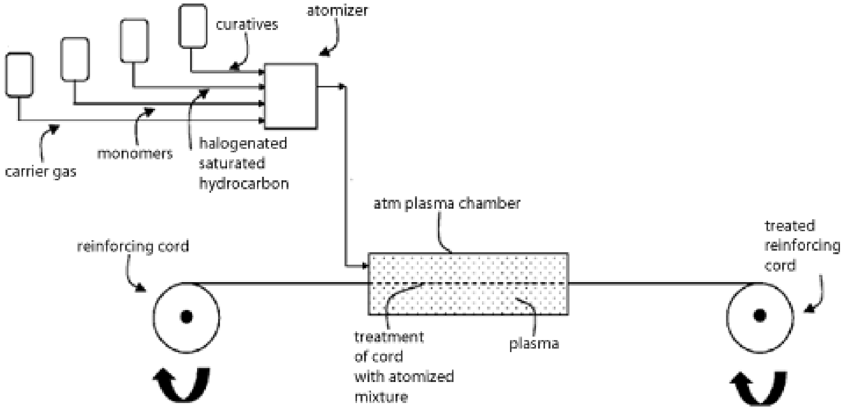


Figure 20: Schema of a processing line as proposed by the patent application US 2011/0241269 [61].

In 2014 another extension of this patent was published [63]. Thereby, a method of treating a cord for reinforcement is disclosed. The method comprises the steps of atomizing a mixture of at least one hydrocarbon sulfide, an organic solvent, and a carrier gas to form an atomized mixture; generating an atmospheric pressure plasma from the atomized mixture; and exposing the reinforcement cord to the atmospheric pressure plasma. The setup is the same as the one shown in Figure 20. Also, a reinforcement cord treated by this method and a reinforced rubber or reinforced elastomer article comprising such a treated cord is disclosed. A method of treating a cord for reinforcement, the method comprising the steps of:

a) atomizing a mixture of at least one hydrocarbon sulfide, an organic solvent, and a carrier gas to form an atomized mixture;
b) generating an atmospheric pressure plasma from the atomized mixture; and
c) exposing the reinforcement cord to the atmospheric pressure plasma.

Clearly, this patent follows the same route as the setup that was developed within the present project. As the publication date is later than the last performed patent search, it was not found and considered during the development phase. The inventive idea to use a hydrocarbon sulfide for the plasma coating is therefore covered by that patent. It remains the question to the patent experts, if the formation of the atomized mixture differs significantly enough, as in thie present project no organic solvent is used.

Another patent application [64, 65] claims a pneumatic tire comprising a tire component having a plurality of individually plasma treated cords applied individually to the tire component. Wherein the plasma treated cords comprise a plasma generated deposition derived from at least one polymerizable monomer. Furthermore, an additional claim covers a finish that is applied to the plasma treated cords during or after a plasma process, where the finish provides tack (adhesion) to the tire component.

Overall the patents and patent applications of Goodyear provide the picture, that the company sees plasma treatment as a key technology for the adhesion of reinforcing cords to rubber compounds. The company is also working on methods and technologies to replace RFL-treatment completely by alternative plasma techniques. Their main aim is to introduce new functional groups with plasma treatment on the surface of the reinforcing cords to achieve chemical bonding to the rubber matrix.

Since the initial literature search at the beginning of this project, the above-mentioned patent application from Goodyear became now a valid US patent (US 8,445,074 B2) filed on 31st of May 2013. However, in the claims only steel cord treatment is mentioned. Therefore, this patent is not affecting the present project. However, the European patent application (EP2371882 A1) of the same subject is still ongoing and it does include polymeric cords. The question is, why the polymeric cords were omitted in the US patent. Either there are other patents or publications that blocked this claim, or Goodyear has reason to believe that a patent in this field is not necessary.

A method for treating and modifying the surface of a polyester fiber was disclosed by Ueno [66]. These polyester fibers show anisotropy in the molten state from subjecting the fiber to a low-temperature plasma irradiation. That treatment can be used to obtain fibers which comprise highly oriented molecules, are highly crystalline and hence exhibit a high tenacity and a high modulus of elasticity. The fibers thus obtained are suitable as a reinforcing material, exhibit an excellent adhesion to matrices to be reinforced and can give a satisfactory strength to the resulting composite material. The plasma treatment was conducted by keeping the pressure in a vessel at 0.2 Torr with helium gas, creating an A.C. voltage of 3.0 kV between the electrodes by means of a gas-tube sign transformer, and moving the fiber at a take-up speed of 2 m/min in the plasma stream. The fiber was irradiated with plasma for about 6 minutes. The pressure inside the vessel was restored to ordinary pressure by using air. The plasma-treated fiber was used to form a pre-preg with an epoxy resin to examine its properties as a composite material.

Riccardi et al. claims in a patent application [67] from 2010 an “Atmospheric-Plasma Processing Method for Processing Materials”. This application is rather unique, as basically the general process of atmospheric plasma treatment is claimed. The claims for example include a plasma processing method for processing materials in general, comprising the step of subjecting at least a surface of a material to be processed to a substantially atmospheric pressure plasma. Furthermore, they claim several gases, processing conditions and plasma setups. But as the claims start at number 31 and the claims from 1 to 30 had to be canceled, it is likely that this application is still under discussion.

A patent application [68] from Stopford et al. about a method of in-line plasma treatment of an optical fiber cable is of interest, because it uses two atmospheric pressure plasma jets in a row to treat reliably the whole surface of a fiber. Additionally, a material dispenser can be installed after the plasma jets to dispense the target material onto the plasma-treated surface. Even though the method has a similar construction to what might be used as a setup in this project, it should not affect this project as it strictly grounds on application to an optical fiber cable.

Mikhael and coworkers filed a patent with the title “Electromagnetic Treatment in Atmospheric-Plasma Coating Process” [69], where an in-line setup is used to coat substrate films or webs. The aim of this invention is the coating with a film, and not the promotion of adhesion, though the approach is interesting for the latter as well (Figure 21). The first step of this in-line process is to apply a plasma treatment (102) and simultaneously deposit a precursor (108) in form of vapor deposition or atomized spraying on the substrate. In a further step, the deposited layer is cured (112) by electron-beam, infrared-light, visible-light or ultraviolet-light radiation. In a third step, a plasma post-treatment (114) is proposed that is used to enhance the properties of the resulting coating.

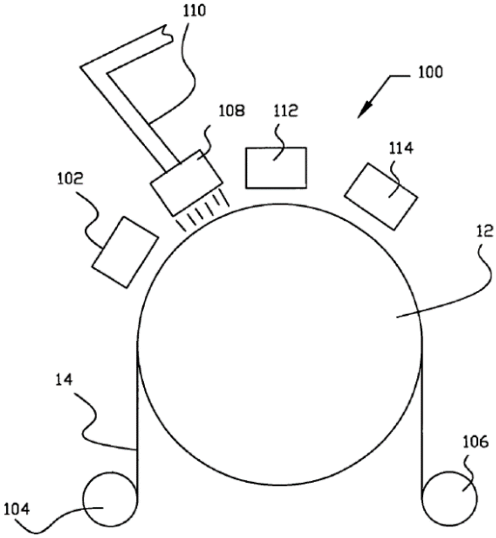


Figure 21: Schematic setup of an in-line atmospheric-plasma coating process [68].

Two more patents cover methods that are directly related to plasma treatment of reinforcing cords and the improvement of adhesion to rubber compounds. Patent WO 2006/135347 [70] by Janypka et al. claims a method of treating a textile material without any preliminary pre-adhesive modification by low temperature plasma at atmospheric pressure. Nitrogen is used as carrier gas and additionally a mixture of propane and butane is fed into a plasma chamber. Plasma polymerization of propane-butane takes place and deposition of a polymer layer at the surface of the treated textile is achieved. The method is claimed for (pulsed) corona and coplanar dielectric barrier discharge, but not for atmospheric pressure plasma jets. The adhesion strength of the treated PET cords compared to standard RFL treatment shows good adhesion values and proves that the method is working.

The other patent, WO2006/088436 A1 [71], is from Mihalik and covers a device for manufacturing rubberized fabric cord, that is suitable to be used as wound overlapping breaker. The wound overlapping belt is a strip of rubberized fabric cord. It is spirally wound onto preceding belt layers and has positive effect on the tire properties. A setup of that device is shown in Figure 22. It consists of an unwinding station (1) for individual cord threads, a plasma unit (2), a transversely arranged rubberizing extruder (3), a cooling unit (4), a longitudinal slitting machine (5) and a winding station for rubberized fabric cord (6). Basically, the patent claims the setup of Figure 22, while it only specifies the conditions of the winding stations used in such an arrangement. Type and specification of the extruder and the plasma unit are not given in the patent.

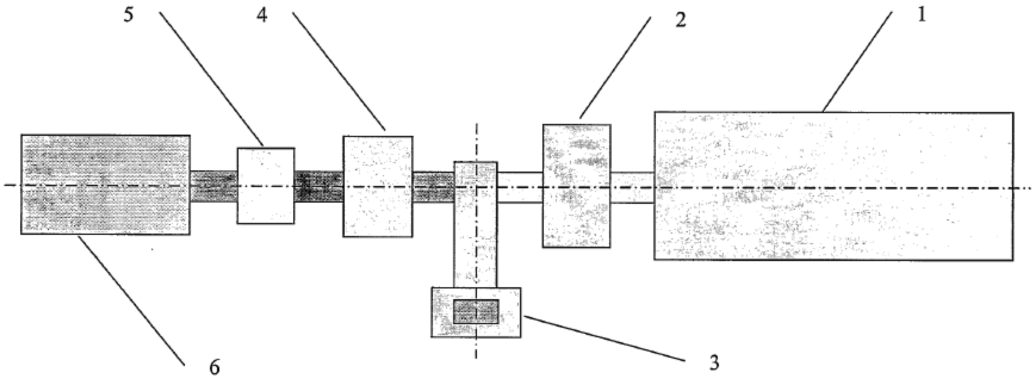
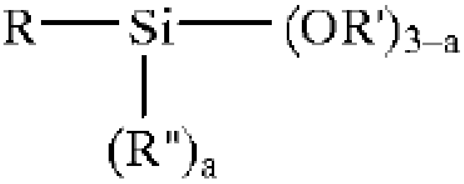


Figure 22: Schematic setup of a device for manufacturing rubberized fabric cord [71].

A patent with focus on an article comprising a rubber/steel body composite was filed by Grimberg [72]. Adhesion promotion is done via a surface activation followed by a surface treatment with a silane. The process comprises the following steps:

- activating the stainless-steel surface of the body, where the steel contains at least 0.02% and at most 0.2 wt% carbon, at least 3 wt% and at most 20 wt% nickel, at least 12 wt% and at most 28 wt% chromium, the sum of the nickel and chromium being at least equal to 20 wt% and at most equal to 35 wt%;
- the structure of the steel comprises at least 20 vol% of martensite and it is without austenite or contains less than 80 vol% thereof;
- treating the surface of the body with at least one starting silane such that the surface is covered with a film constituted exclusively, or substantially exclusively, of one or more silanes characterized by the following formula:



$$R-\mathrm{Si}(R'')_a-(OR')_{3-a}$$

in which R represents an organic radical that is capable of reacting with at least one element of the composition: (a) each OR‘ represents a group capable of reacting with an oxide or hydroxide of the surface of the stainless steel; and (b) each R“ represents, independently, hydrogen, a cyclic or acyclic organic radical, or a halogen; and *a* – which may be zero – is equal to at most 2;

- placing the treated surface of the body in direct contact with the composition; and curing the composition.

While this patent does not compete with the aim of the present project, the patent description includes plasma as possible surface activation step and the use of a silane thereafter. Due to that, the novelty of the treatment performed in the present project might be compromised.

2.9.2 Plasma equipment

As shown in chapter 2.8, it is possible to obtain atmospheric plasma discharges by different arrangements. Different approaches can be found on the market and in the literature that follow the requirements set by the type of application. A common solution are the atmospheric pressure plasma jets (APPJ), which are realized nowadays in handy plug&play devices. They usually consist of a main unit which is connected to all necessary supplements and is the central control station. Attached to that main unit are one or more plasma jets. The plasma is guided through a nozzle onto the surface that is to be treated. Usually they are installed in industrial in-line treatment arrangements. Either it is controlled in an automated way by a robot-assisted process or installed into a processing line as a fixed treatment unit. Standard processing gas is air, but most of them can handle nitrogen as well. Other processing gases are in general possible, but are not a standard technique. The technological risk is low as the system is ready to be used out of the box. Furthermore, these setups claim to have low operating costs, especially for treatments with air as processing gas. It needs to be mentioned that the nozzle of an APPJ equipment undergoes wear and must be replaced regularly.

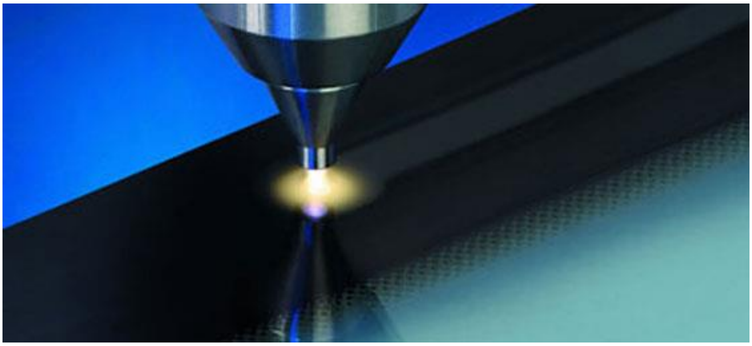


Figure 23: Typical treatment procedure with APPJ technology [15].

The plasma output (see **Figure 23**) of APPJ's is considered to be stable and therefore produces a constant surface quality. The high reliability of such a surface treatment is a major advantage of this technique and helps to lower the production costs. In case of a cord treatment it is possible to use more than one plasma jet for the surface activation. Doing so ensures a proper and uniform treatment of the whole surface, as the treatment with a single exhaust nozzle would create a shadow on the opposite cord surface and cause a non-uniform treatment. A drawback of such a treatment is, that a scale up would require an increased number of nozzles and decreases the efficiency compared to a DBD system. Alternatively, the plasma jet nozzle could eject the ionized gas into a closed chamber, where the excited particles are reflected and then treat the opposite cord surface as well.

A setup based on the MonoJet from Advanced Machines was used by Teijin [73] and is shown in Figure 24. It is questionable, if that setup is the best possible solution for a proper treatment of the cord surface. Though a plasma jet produces a homogeneous and uniform discharge that is injected with high velocity, the cord surface could be non-uniformly treated as the reflected stream may be turbulent.

APPJ-equipment and support are available from several suppliers on the market. The investment costs for a plug&play system range from 10.000 to 30.000 € with a delivery time between 4 to 8 weeks. Rental of such devises is also possible, then the costs are between 20 to 100 € per calendar day with a delivery time of 4 weeks. A disadvantage of the commercially available plasma nozzles is, that the exhausted plasma flame has a diameter of about 5 mm. There are rotational nozzles build for flat surface treatments which increase the size of treated area. This approach is not suitable for cord treatments, as each part of the cord needs to be treated as equally as possible. Therefore, the current plasma nozzles are suitable for a single cord treatment, but not for a possible upscale of test equipment. PlasmaTreat GmbH mentioned, that there is a new nozzle generation under development which delivers a much broader but still constant and equal plasma flame. Such a nozzle system would make it possible to treat several cords simultaneously, a mandatory feature for this technique to be suitable for an industrial scale production line.

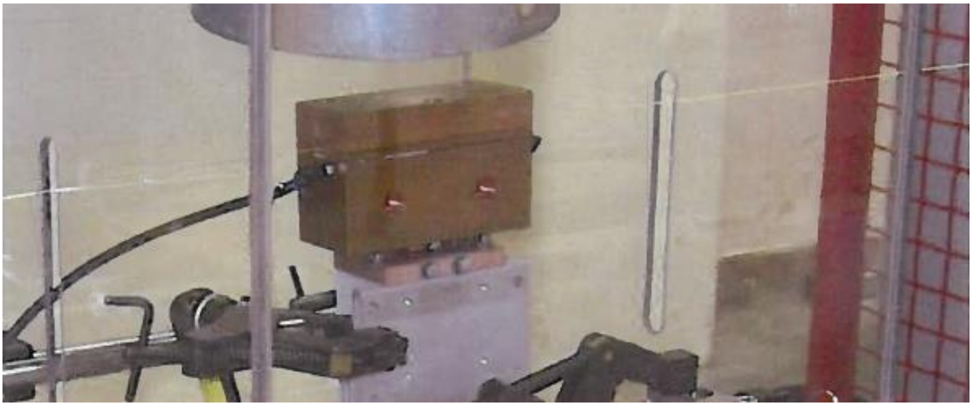


Figure 24: Close-up of a plasma setup where the ionized gas is injected into a small metal chamber [73].

Another widely used technique is the dielectric barrier discharge. A strong advantage of this technique is, that results and optimizations obtained with a laboratory-scale DBD: see Figure 25, can often be more easily transferred to large industrial-scale DBD installations. When set to a glow discharge mode, a cord- or filament-treatment with a DBD unit can be performed very homogeneously, as the cord is treated uniformly from all sides. This also eliminates the need to install additional equipment to ensure a proper treatment like in the case of APPJ. Another advantage of a DBD and its volume discharge is the possibility to run more than one cord through the same plasma, which increases the efficiency of the process significantly. Furthermore, if both electrodes of the setup are protected by dielectric layers, the occurrence of wear effects can be prevented and the system is nearly maintenance-free. A drawback of this technique is that the discharge tends to be less stable compared to the APPJ-system. To maintain a reliable homogeneous glow discharge under atmospheric conditions is a difficult task. Small fluctuations in the amplitude or repetition of the frequency can cause a transition into a more stable filamentary discharge mode [74].

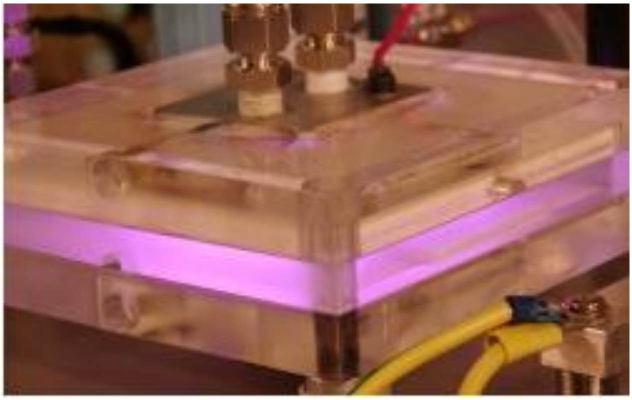


Figure 25: Example of a dielectric barrier discharge at atmospheric pressure [75].

Vito, a Belgium based technology development company, is offering plasma treatment systems based on the DBD technique. They claim, that the direct plasma contact limits the gas consumption and allows high speed processing at working temperatures of 25 - 120 ˚C [76]. The “Plasmazone” called technology is suitable for cleaning, activation and coating applications. It offers a wide voltage and frequency range from each 1 -100 kV and kHz, respectively.

A self-built atmospheric pressure plasma reactor focused on treatment of cords has been built by Prof. Hudec and his group at the University of Bratislava, Slovakia [77]. As it uses a high voltage of about 25 kV and a low frequency of 100 Hz, this reactor has similar parameters to a DBD-equipment.

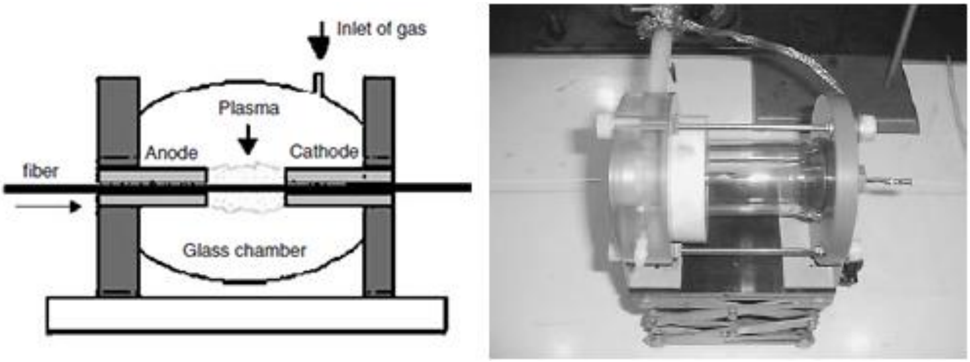


Figure 26: Schematic drawing and a picture of a plasma reactor build by Hudec et al [77].

In Figure 26, the reactor is shown. Clearly visible is, that the cord runs through the center of the electrodes while being protected by a nitrogen atmosphere that is present in the glass chamber. Unlike a plasma jet, where only the gas outlet touches the cord, in this case the cord encounters the highly aggressive species of such a plasma. Hudec et al. achieved adhesion values with plasma treated polyester cords, which were similar to the ones of RFL coated polyester fibers. However, despite these promising results, the project was not continued.

2.10 SUMMARY AND CONCLUDING REMARKS

Polymeric reinforcing cords do not adhere well to rubber compounds without further treatment. The lack of adhesion is caused by polar and inert surface properties, the smooth surface and the high modulus of the cord. To reach an appropriate level of adhesion it is necessary to apply an adhesion promoting treatment. Polyamide and rayon cords undergo a dip process where a RFL coating is applied, which migrates into the upper layers of the cords and is cured with a heat treatment. Other cords have stronger inert properties and less functional groups available. In those cases, a two-step treatment must be applied: First an epoxy coating is subjected, followed by the standard RFL-treatment.

Despite the fact, that the RFL-treatment dates back to the 1930's, it is still the standard treatment and commonly used in the industry. Since then the development of a suitable alternative was the subject of many research programs. However, no other adhesive system for polymeric cords could reach the same level of adhesion or managed to surpass it. This demonstrates nicely the strong advantages of the RFL dip system and how well it is adapted to the unique needs of an adhesive between polymeric cords and rubber. So, where is the driving force for a replacement coming from? The main reason to look for alternatives is in fact the risk, that the legislation may act against key ingredients of the RFL-dip because of their toxicity. One route to solve that problem will certainly be, that other less problematic chemicals will be used in a similar process. Another way out might be the development of suitable alternatives that take completely new routes.

One promising candidate is plasma treatment. Its ability to perform surface treatments which chemically alter the properties makes it very suitable. Furthermore, the plasma technique is nowadays small and compact as well as applicable at atmospheric conditions. This makes it very interesting for industrial applications. The framework in this project was to apply plasma treatment to single-end cord. The literature research made it obvious, that this approach is not entirely new and some researcher have already contributed to this research field. However, these approaches never reached the level of industrial application. Nevertheless, there is an immense potential to further investigate this technique with the aim to promote adhesion between cord and rubber.

CHAPTER 3

Concept of the plasma line: selection of plasma equipment, setup of the line and basic development of the treatment process.

This chapter describes the concept and the basic development of the plasma line. The line was designed to promote adhesion between rubber and cord by a plasma-cleaning and coating step. The basic concept consists of a winding unit, a plasma reactor and an extruder with crosshead for rubberizing the treated cords. The process line was further upgraded during the project in order to improve the treatment conditions in terms of efficiency and enhancement of the cord-rubber adhesion. Besides, the periphery of the plasma treatment line was optimized during the development and testing stage and was adapted to new requirements.

3.1 PROBLEM STATEMENT

The scope of this project was to promote adhesion of polymeric cords to elastomers with the help of plasma technique. Adhesion between different components in a composite like a tire is crucial, as it allows forces to be transmitted within the composite and thus increases strength and provides specific properties. The final goal is to integrate this technology into a tire-building line, therefore the materials used in this project should be of such a kind that they are suitable for an industrial application: The reinforcing cord should be in the form of a single-end type, meaning that the single cords are treated and not a fabric woven from the single cords. Using single-end cords reduces the requirements for the plasma equipment, because a relatively small surface area needs to be treated at a time.

These constrains were defined in order to develop a process that finally is of practical use in an industrial environment and is not only interesting from an academic point of view. Two further requirements were aiming in similar direction: one is the in-line capability of the process, which means no discontinuous process steps can be used, and the other one is that the process should run under atmospheric pressure conditions.

3.2 CONCEPT AND DEVELOPMENT OF THE PLASMA LINE

With that framework in mind, an initial layout of the plasma treatment line was developed. The following main components were necessary to meet the requirements:

- Winding unit suitable for single-end cord;
- Tension control system;
- Plasma treatment unit incl. generator;
- Auxiliary equipment like power supply, air pressure, etc.

The winding equipment simulates surrounding processing steps in an industrial setup, where the single-end cord comes from a former step, runs through the plasma unit and continues thereafter in another processing step. The winding unit should have the ability to run at a wide range of pulling speeds in order to simulate low speeds for testing purposes and higher speeds for production simulations. A tension control system is necessary to keep an appropriate tension on the cord, independent from the actual speed of the cord. The plasma treatment itself, as well as its requirements and dimensions, are strongly depending on the type of plasma that is going to be used.

3.2.1 The plasma unit

This is the core unit of the treatment line, and two options for the plasma units were intensively studied:

- A parallel installed pair of electrodes using a Dielectric Barrier Discharge (DBD) design;
- A plasma nozzle, also called Atmospheric Pressure Plasma Jet (APPJ).

A DBD design would have the advantage of offering the possibility to simultaneously treat multiple cords, and that the dimension of the electrodes can be used as another factor to adjust the treatment time besides the speed of the cord itself. Its major drawback is, that these electrodes have to be tailored for a specific application, making it rather difficult to be used for this industrial application. Besides, as this project is focused on the application of a plasma device and not on its specific development, the latter can indeed be considered as a significant disadvantage. An APPJ instead is commercially available as test/lab-scale plasma treatment equipment as well for industrial applications. However, due to the thin plasma output diameter, which is about 5 mm, the treatment of multiple cords is not possible. However, for a proof of concept, a lab-scale single cord plasma treatment setup is suitable.

These were the main criteria for the choice of a plasma option:

- Suitable for an atmospheric non-thermal plasma;
- Able to treat a cord in an in-line processing environment;
- Operation at nearly room temperature conditions;
- Surface cleaning with inert gas to avoid oxidation;
- No negative influence on the cord properties;
- Deposition of functional groups on the cord surface.

Both, a DBD as well as an APPJ plasma system, can fulfill these criteria. The decision was then made to use an APPJ setup, as this was commercially available as a well-established system with low financial and technical risk.

The APPJ setup was consisting of a Plasmatreat FG1001 generator and two PFW-10 plasma nozzles, but it was not equipped with a dosing unit for chemicals, used as precursors in order to perform surface coatings. Still, the FG1001 with a power input of about 2 kW could be used for cleaning and etching purposes. Initial tests comprised a general study of the cord behavior when plasma-treated, and of the arrangements within a plasma treatment line.

3.2.2 Layout and fine tuning of the first experimental plasma line

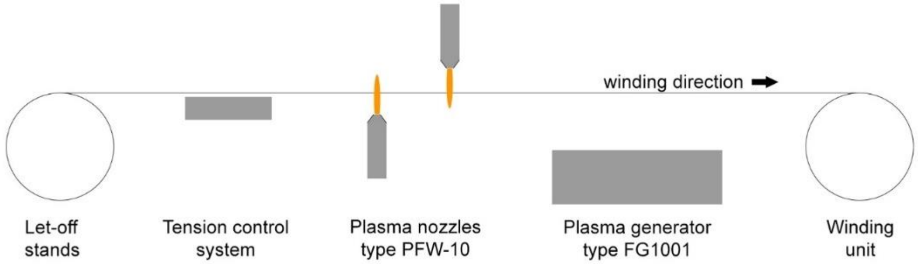


Figure 27: Initial test setup configuration with Plasmatreat FG1001 plasma unit.

In Figure 27, the initial configuration of the plasma treatment line is shown. It consists of the following components:

- Let-off stands where the raw cord material is stored;
- McCoy Single End Tension Stand Model 21T with load cell tension controller;
- Plasmatreat FG1001 plasma generator (2 kW) with two PFW-10 plasma nozzles attached;
- And a computer-controlled winding unit with freely settable winding speed built by VMI.

This initial setup was used to obtain experience with the general handling of polymeric cords and their behavior in a plasma. The operational windows of several parameters had to be defined at first instance:

Cord speed - The minimum cord speed, for example, was determined to see at which speed, thus treatment time, damage of the surface as well as of the cord as such is detectable. Polyester showed significant damage and brittleness on its surface when plasma-treated with speeds lower than 5 m/s. A further reduction of the cord speed caused breaking of the cord. These tests showed, that a plasma treatment of polymeric cords can affect the bulk properties of the cord. Plasma treatment in general is well-known as a surface treatment method, but in this case, the small diameter of the cords of less than 1 mm leads to changes in the bulk properties of the cords as well. Therefore, the minimum treatment speed cannot be determined just by checking the cord’s surface for damage, but mechanical properties must be considered as well.

Plasma generator parameters - An analysis of the plasma generator parameters was performed. However, it turned out that the FG1001 has only a stable output at its maximum power settings. That was achieved at 280 V and 4,7 A, which is equal to a power output of 1,3 kW. Due to that, a Design of Experiments (DoE) setup to study the significance of the generator parameters was not possible. The ionization gas was oil-free pressurized air delivered from a compressor. Tests with other gases to ignite the plasma were not successful. Next to the fact, that this plasma unit is not suitable for plasma polymerization, the choice of useable ionization gases was limited to air only, and a variation of the plasma parameters caused an unstable plasma output. These substantial limitations made clear, that a more advanced plasma unit was necessary.

Nozzle position - One issue that became obvious during these initial tests was, that the cord was rotating while being pulled through the plasma line. At first glance, this seemed not to be a problem, but with the two nozzles installed in a row like shown in Figure 27, an equal surface treatment could not be guaranteed. To prevent the rotational movement of the cord, a rather complex technical solution would have been necessary: this would not be desirable for a later production setup. Therefore, the nozzles were repositioned to solve the problem. They were positioned with focus onto the same spot on the cord with a certain angle towards the direction the cord (shown in Figure 28). In such an arrangement, both plasma flames were combined to one larger plasma treatment zone. This installation ensured a significantly improved homogenous plasma treatment of the polymeric cord. The added intensity of both APPJ’s treating the cord at the same time became a disadvantage of that solution, but it was compensated by reducing the power output of the generator, increasing the cord speed and adjusting the distance between nozzle and cord.

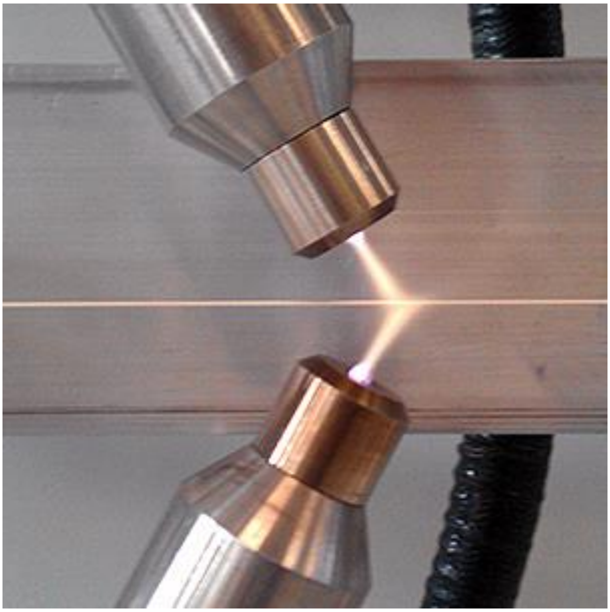


Figure 28: Illustration of a combined plasma zone to ensure an equal treatment of the whole cord surface.

Closed reactor chamber - Along with the repositioning of the nozzles, a cabinet for the plasma treatment was also introduced in combination with a fume exhaust extraction system from Nederman Nederland B.V. The cabinet improved the safety when the plasma unit was running and prevented exhaust gases getting into the surrounding environment. Besides, this closed reaction chamber allowed to work with protective gases and gave a better control of the plasma treatment conditions. The reconfigured second version of the plasma line is shown in Figure 29.

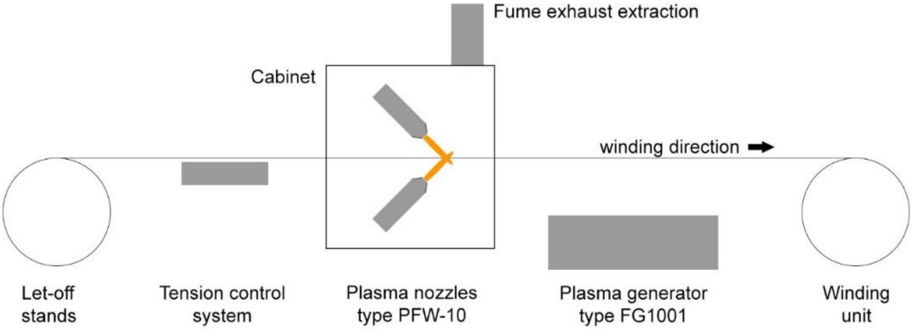


Figure 29: Second configuration of plasma line with improved treatment and controlled exhaust extraction.

This setup was used to further study the effect that plasma treatment has in general on polymeric cords. To quantify this effect, the following three parameters were analyzed by tensile test measurements on the cords:

- Elongation at break (EAB);
- Force at break (FAB);
- Elongation at 45 N (EA45N).

The effect of plasma treatment was also measured in terms of change of surface energy using a contact angle measurement device. The results of these measurements will be described later in Chapter 7.

3.2.3 Choice of the plasma polymerization unit

The setup in Figure 29 was used to determine what kind of additional equipment was needed. From literature it is known, that polymeric cords do have surface contaminations that hinder the adhesion to rubber. These contaminations are mainly processing aids in form of oil which are used during the cord production process. Therefore, removal of these contaminations is a necessity, and this can be done by the existing FG1001 APPJ unit. The new plasma unit was chosen to be suitable for different kind of plasma treatments, and would be used as the actual coating unit. This results in a setup, where first a pair of plasma jets will clean the cord surface and after a short distance along the cord, a second pair of plasma jets will perform the plasma coating. The additional plasma equipment consists of the following components:

- Plasmatreat FG5001 plasma generator;
- Plasma polymerization unit PAD1;
- PFW10-PAD plasma jets.

The FG5001 plasma generator is a much more advanced, digital successor of the FG1001 and can provide a plasma output of up to 1 kW. Furthermore, this generator provides more variable plasma parameters, so that a fine tuning of the plasma properties is possible. In order to be able to deposit a coating, a control unit is necessary that supplies and evaporates the chemicals that are used for the plasma coating process. This unit is called PAD1. It is a computer controlled device (see **Figure 30** left), that controls the ionization and carrier gas flows, the precursor flow rate as well as the evaporation temperature which can be as high as 250 ºC. The plasma deposition jets are still PFW-10 versions, like the APPJ’s of the cleaning plasma unit. However, they are modified to be able to deposit a precursor on a substrate's surface. The actual evaporator of the precursor is mounted closely to the jets, so that the precursor can be injected into the plasma right after evaporation.

Figure 30 : PAD1 plasma polymerization unit (left) and FG5001 plasma generator (right) [courtesy of Plasmatreat GmbH].

3.2.4 Setup of the plasma line with cleaning and polymerization unit

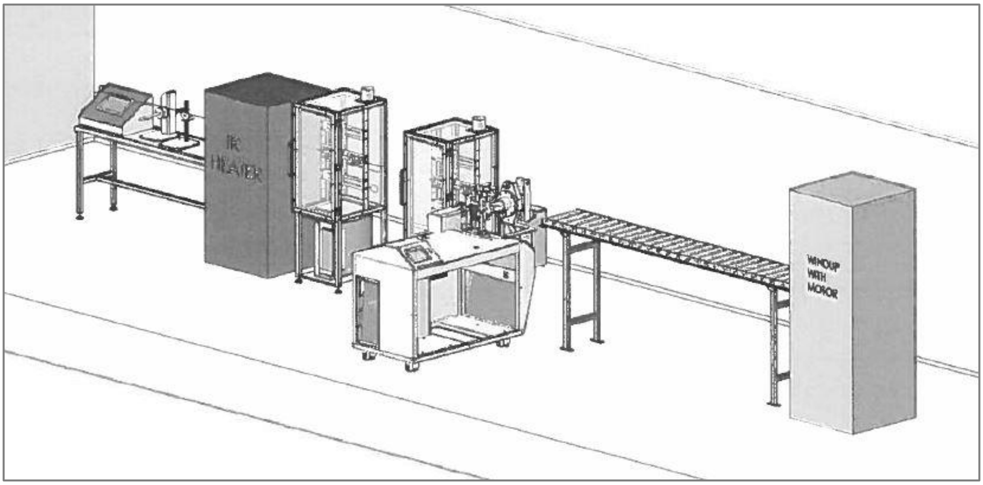


Figure 31: Layout of the plasma line with two treatment chambers for each plasma unit.

The line with two plasma treatment steps was constructed according to the configuration shown in Figure 31. It consisted of the following devices:

- McCoy Single End Tension Stand Model 21T with load cell tension controller;
- IR heater Mo-El Halogen IR Fiore 1800;
- Plasma cleaning unit (CU) consisting of a Plasmatreat FG1001 plasma generator with two PFW10 plasma nozzles;
- Plasma polymerization unit (PU) based on a Plasmatreat FG5001 plasma generator with two PFW10-PAD plasma nozzles and a precursor evaporation and dosing unit PAD1;
- Both plasma units, each installed in a separate cabinet, are attached to an exhaust extraction system by Nederman, which can create a slight underpressure environment inside the cabinets;
- Planetruder S extruder by VMI with attached crosshead for single-end cord rubberization;
- Computer-controlled winding unit with freely scalable winding speed.

The more advanced second plasma generator FG5001 delivers not only more power, it also enables the operator to choose more accurate settings. This is important in order to control the plasma output in a way, that the optimal conditions for the plasma polymerization process can be chosen accurately. Otherwise, there is a possibility that the precursor gets atomized and thus destroyed in the plasma. It will quickly recombine, but the functional groups might have vanished, and the precursor cannot react with the moieties on the cord surface anymore. Furthermore, the FG5001 generator is controlled by the same software that runs the PAD1 unit. That means that the whole plasma coating process is controlled by one system, which helps to simplify the process significantly.

Rubberizing of the plasma-treated cord - The addition of the extruder to the plasma line was owed to the fact, that a freshly treated surface contains a considerable number of active moieties. These will react with reactants in the environment during a certain period of time after the plasma treatment. If the cord is wound up after the treatment without further protection, it will react with oxygen present in the air. This reaction inhibits adhesion, as the active radicals and functional groups on the cord surface are consumed before they can get into contact with rubber. Therefore, it was considered to incorporate an extruder with crosshead, which enables the setup to bring the plasma treated cord in contact with the rubber in a very early stage. Remaining active species on the cord surface won’t be able to react with oxygen anymore and will not get passivated due to the protective coating.

The cord enters the extruder head on one side through a small opening (diameter: 1 mm) matching the diameter of the cord. Inside the head, a rubber reservoir is fed by two streams from the extruder. While the extruder is one of the smallest types available on the market, it still delivers a much higher throughput of rubber than necessary to cover the cord with a protective rubber layer. A bypass is used to remove excessive rubber from the crosshead and functions as a pressure control valve. Via the screw speed the temperature and viscosity of the rubber compound are indirectly adjustable. A die on the other side of the crosshead defines the actual coating of the cord. Its diameter is designed corresponding to the actual diameter of the cord and is in fact 1 mm as well. Rubberizing the cord is a suitable way to protect the plasma treated surface from the environment and can stay as protective media till vulcanization of the final product. One small extra step is the use of PE foil to separate the cord layers when they are wound up at the end of the treatment line. Without that extra step, the uncured rubber would stick together and further processing would not be possible. The rubberizing parameters were optimized at a later stage and will be described more in detail in Paragraph 3.2.5.

Basically, this configuration of the plasma line makes it possible to perform three treatment steps which are shown in **Figure 32.** In the first section, the cord gets cleaned and dried by a pair of plasma jets powered by the FG1001 (a). Shortly after, a second plasma treatment step for deposition of a precursor (b) is performed. This treatment step performs the actual chemical modification within this process. The precursor creates a very thin layer on the cord surface introducing new functional groups that can participate in vulcanization and makes the surface chemistry resemble the elastomers in the rubber. Finally, the cord runs through the crosshead extruder (c) to ensure the best possible adhesion to rubber without a possible contamination.

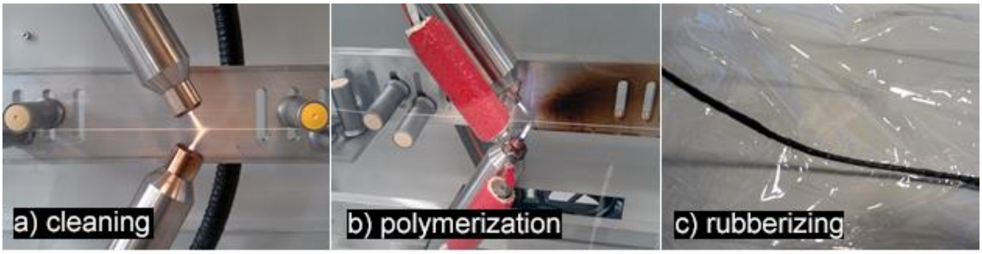


Figure 32: Image of the plasma nozzles of a) the cleaning unit and b) the polymerization unit. c) shows what the rubberized polymeric cord looks like after passing the extruder section.

Drying of the cord before plasma treatment – Depending on the type of polymeric cord, it might be necessary to dry the cord before exposing it to the plasma. The reason is the hydrophilic character of some cords and the moisture uptake from the environment that comes along with this. In first instance an IR-heater, type Mo-El Halogen IR Fiore 1800, was introduced into the line, but with the regular cord speed the heater was not able to reduce the amount of moisture sufficiently. To overcome this problem, it was discussed if the FG1001 plasma jets can dry the cords at the same time where the jets decontaminate the cord. The temperature of the plasma flame was quoted by the supplier to be approximately 150 °C, and the exhaust through which the cord must pass after the plasma treatment are very likely reducing the moisture content of the cord significantly. However, it turned out to be very difficult to determine how much moisture was evaporated. TGA measurements were preformed, but those could not measure any significant weight loss difference between dried and non-dried samples. This was caused by a practical limitation: it took too much time to handle the samples and store them in a dry environment immediately after the plasma treatment was performed. The process of the cord to take up moisture from the environment is rapid, and because of the misbalance in humidity between cord and environment the driving force is huge. In fact, it was only a matter of seconds to moisturize the dried cord again. This behavior was proven by a laboratory test, where a dried cord sample was taken from a 70 °C warm air oven and put under atmospheric conditions on a sensitive balance. The strongest increase in weight was noticeable directly at the beginning, and the cord sample weight became steady soon after the start of the test.

As drying by an IR-heater was not sufficient, in the new setup an oven was installed before the unwinding unit. This addition of an oven turned out to be a suitable solution to the moisture problem. A laboratory oven was installed at the beginning of the line. It could host the whole spool of cord and keep it dry at a set temperature during operation of the plasma line. The cord was guided through a small exit on the backside of the oven to supply the plasma line and the IR-heater was used to keep the moisture uptake from the environment as low as possible while the cord was transported to the plasma jets. When operating the plasma line with air as ionization gas, moisture in the cord might not be a problem, as during the treatment a considerable amount of oxygen will be present anyway. However, if another ionization gas is used and the presence of oxygen should be avoided, then the residual moisture in the cord can be a source of oxygen. In case that the treatment is supposed to be oxygen free, sufficient drying of the cord is mandatory.

Finally, the Rayon coil was installed in an oven, which is preheating the rayon cord to 80 ˚C for 1 h before actual usage. Additionally, the distance from the unwinding unit to the plasma treatment cabinet was covered by an infrared heater. This measure was necessary to avoid moisture uptake of the freshly dried Rayon cord before the plasma treatment.

Nozzle position - It became clear, that the distance between the two sets of plasma jets could be reduced to a narrower gap than in the first setup of the line. The gap was reduced from about 1 meter, where both plasma units had their own cabinet, to 15 cm in a single cabinet. This also enhanced the suction system, as now both units were in the same reduced-pressure environment. The new configuration of the plasma nozzles is shown in Figure 33, featuring a much sharper angle with the cord and thus a larger plasma region along the cord.

Figure 33: Advanced plasma nozzle configuration.

Oxygen-free atmosphere - In this development stage, a Design of Experiments (DoE) run was performed to determine the important process parameters of the line, see Chapter 4. The main outcome was, that there were no significant differences between the chosen parameter settings. The only conclusion that could be drawn, was that the presence of oxygen had a negative effect on the adhesion levels. Oxygen reacts with the active radicals on the cord surface, which reduces the reactivity towards rubber and makes the cord surface more polar and, therefore, less compatible with the rubber. The solution is to use a protective gas atmosphere. This can be realized by using nitrogen to flush all other gas molecules out and put the plasma chamber under a slight overpressure. This has the advantage that the chamber doesn’t have to be very air tight, as it is surrounded by a lower-pressure environment.

In first instance, a rather simply designed chamber was built as shown in Figure 8. However, during the initial tests with this new setup it became obvious, that temperature and pressure stability were not good enough to maintain the elevated temperatures of the APPJs and the pressure of the protective atmosphere for longer periods.

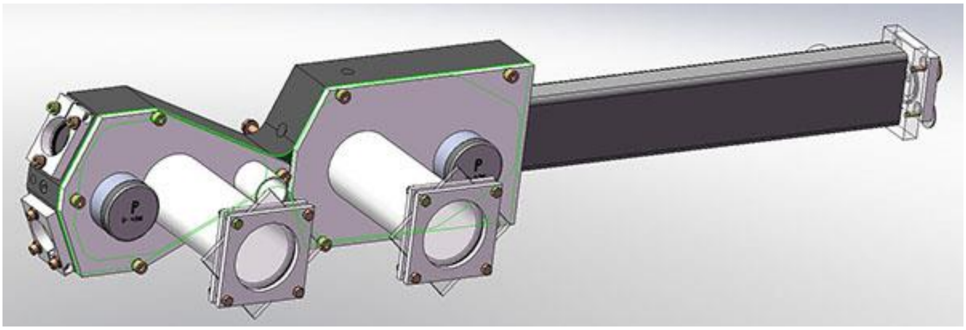


Figure 34: CAD design of the overpressure plasma chamber. On the left-hand side, the first part of the plasma chamber is located where the CU nozzles are installed. In the middle is the actual plasma polymerization section and on the right-hand side the extended treatment zone, which protects the cord before entering the extruder.

3.2.5 Final layout of the plasma chamber

A much more sophisticated approach was necessary to achieve the desired plasma conditions: see Figure 34. The following requirements were stated for the design of the overpressure plasma chamber:

- Separated treatment chambers for each treatment section (CU, PU);
- Withstanding high temperatures for long periods;
- Keeping a constant overpressure level;
- Good sealing properties to reduce the amount of nitrogen lost;
- Controlled gas flow;
- Optimized precursor flow;
- Sharper angled position of the APPJs;
- Alternative possibility to inject a chemical vapor which is not plasma-activated, but able to react with the activated cord;
- Good accessibility for maintenance;
- Adjustable distance CU-nozzle to cord.

The latter is not possible for the plasma polymerization PU-nozzle due to the evaporator attached to it. The shape doesn't allow it to be inside the sealed chamber.

To fulfill these requirements, a stainless-steel construction was chosen. To be able to make it as gas-tight as possible and to maintain a constant pressure, the chamber was made out of one block and covered by a rubber-sealed lid. This reduces the number of welded joints and, therefore, gives less room for leakages. The cord enters and exits the chamber via small plugs which are just slightly larger than the cord diameter. Inside the chamber, no cord guidance is possible. Because of that, the chamber needs to be exactly aligned with the winding equipment and the crosshead of the extruder. The suction system consists of valves, which allow to adjust the pressure of both treatment chambers. This helps to avoid gas flows from one chamber to the other, and is also useful for controlling the overpressure inside the plasma reactor.

To optimize the use of the precursors, the angle between each nozzle-pair was further sharpened, in particular to narrow the joint plasma zone and to lengthen it around the cord: see Figure 35. Besides the APPJ-angle, also the layout of the reaction chamber itself as well as the positioning of the suction system was done in a way, that the cord could be kept as long as possible within the precursor flow zone. Therefore, the second chamber, where the actual chemical treatment takes place, featured a long extension of the chamber towards the crosshead of the extruder. In fact, the plasma nozzles inject the nitrogen gas used for the plasma ignition plus the precursor and establish a nitrogen/chemical vapor atmosphere within the chamber. The suction of the exhaust is located in the opposite position. This creates a gas and precursor flow along the cord, which extends the treatment zone and protects the freshly treated cord until it enters the crosshead where the protective rubber layer is applied.

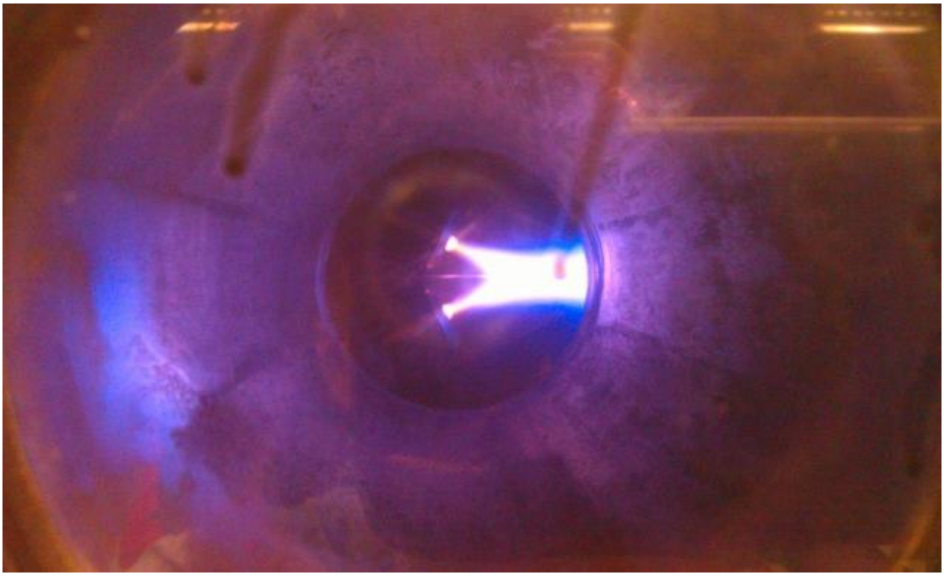


Figure 35: Combined plasma flame inside the treatment chamber. The cord is best visible as a white line in the middle of both plasma jets before it enters the plasma glow.

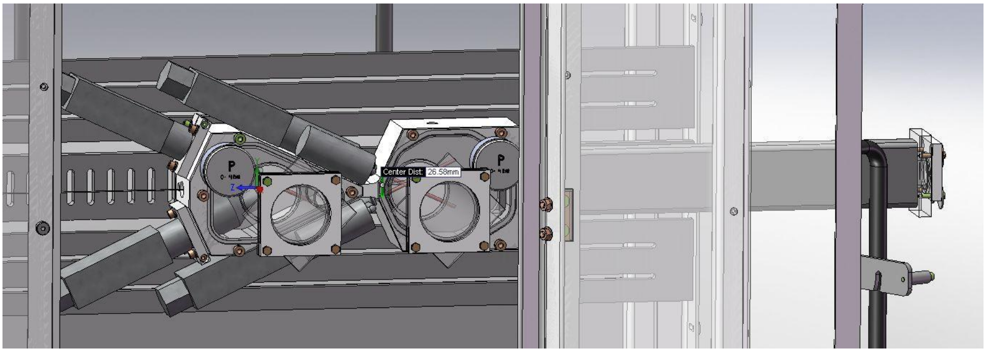


Figure 36: Final CAD design of the overpressure plasma chamber with the four APPJs in place.

Figure 36 shows the final CAD design featuring all the required abilities. It is temperature resistant, has only a few welding joints, can control the overpressure level and, most important, gives the desired gas and precursor flow that is expected to enhance the efficiency and ensures that the plasma treated cord is not contaminated before the rubber coating is applied. As will be discussed in detail in Chapters 4 and 5, the new setup of the plasma reactor greatly improved the adhesion values. The developed concept of a protective gas atmosphere was successful, and the assumption that the presence of oxygen is indeed harmful for the treatment process was proven.

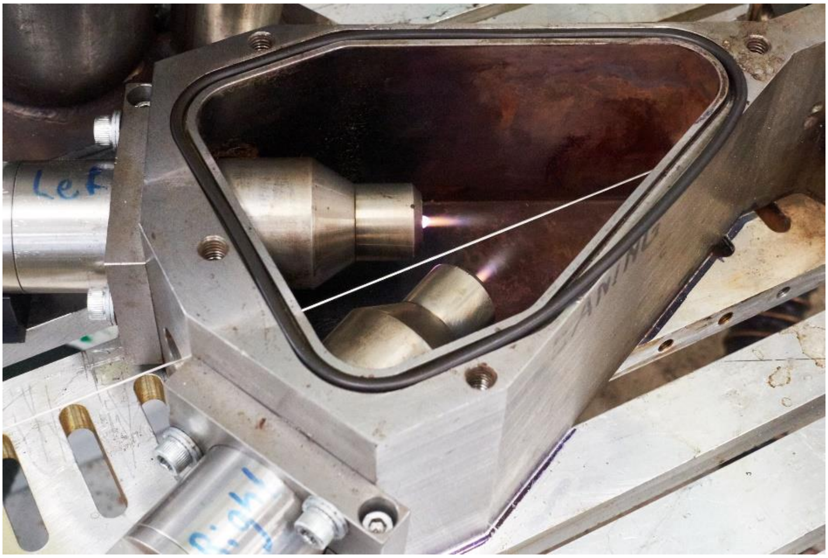


Figure 37: Close-up view of the first APPJ pair that is being used for decontamination purposes.

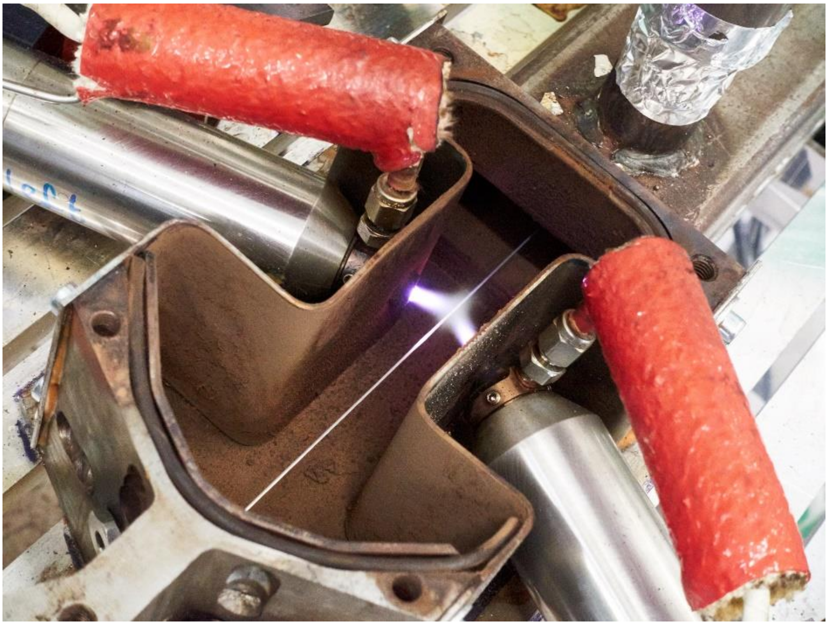


Figure 38: Close-up of the actual plasma deposition chamber. Each APPJ has an evaporation unit attached.

Figure 37 shows the inside of the first plasma chamber. The two APPJ's are installed with a fixed angle allowing them to blow the plasma stream alongside the cord. When the chamber is closed and filled with nitrogen, a large glow discharge: see Figure 35, is established with the cord running through the middle of it. Therefore, the cord is exposed to such a plasma for several centimeters of travelling distance. As the plasma flames of the APPJ's combine during operation, the nozzle-to-cord distance is expected to be of less importance. The chamber is designed in such a way, that this distance can be adjusted easily.

The final status of the plasma polymerization chamber is shown in Figure 38. It was altered from the original plan in several ways. The aim was to improve the treatment conditions after the difficulties encountered during the DoE, where the differences between the minus and plus settings were negligible, and an expansion of the parameter range was not possible. If the generator power cannot significantly be increased anymore, a stronger plasma can only be realized by reducing the gap between the plasma nozzle and the cord. However, due to the attached evaporators, the chamber was designed with a fixed nozzle position. Therefore, the sidewalls had to be removed and replaced by a new layout closer to the cord. That layout enabled a positioning of the plasma jets much closer to the cord and with a freely adjustable angle, which even allowed to direct the plasma stream opposite to the direction of the pulling of the cord. Furthermore, the exhaust suction position had been relocated close to the actual spot where the plasma hits the cord. Initially, it was expected that the best position for the exhaust would be at the very end of the treatment chamber. In actual practice, it turned out that over time the treatment became less efficient, noticed by decreasing adhesion values, while the plasma treatment was ongoing. This is in contrast to the expectation that a longer residence time of the cord in the plasma gases would improve the efficiency. Actual practice showed, that the effect was negative for the adhesion values. A possible explanation for this effect is secondary reactions taking place within the plasma-activated gas resulting in less active species.

Figure 39 shows on the left-hand side the precursor pumps that is responsible for delivering a steady precursor stream to the APPJ's. It pumps the precursor to the evaporator, where the chemicals get heated up to the set temperature. Once it is vaporized, a nitrogen stream takes it along into the APPJ where the precursor is exposed to the plasma. The picture on the right-hand side displays the control units for the gas pressure, which can be adjusted and monitored via the operating software.

Figure 39: Precursor pump (left) and gas pressure gauges (right) for carrier and ionization gas supply.

Plasma parameter range - Even though the adhesion values improved significantly right from the start with the new chamber, the results did not reach values as good as RFL-treated cord. To better understand how the performance could further be improved, another DoE was performed with a new setup, again with the aim to analyze which parameters are of importance. The following three parameters were considered in a 2^3 factorial design plan:

- Precursor flow rate;
- Plasma power;
- Plasma cycle time.

The outcome of this study was, that the maximum of each of these three parameters together resulted in the best adhesion, any other combination of these factors ultimately leads to a significant reduction in adhesion. This result of the DoE had the disadvantage, that an optimization of the parameters was not possible under these circumstances. An increase of the plasma cycle time beyond 100 % is clearly not possible as this value describes what percentage of the total cycle time the plasma is ignited and can create new, highly charged electrons, ions and radicals. The remaining cycle time the generator will not apply any voltage to the electrodes; thus, the plasma is off. The plasma power and precursor flow rate however can be increased by tuning the hardware, the plasma generator or precursor pump, respectively. An enhancement of these performance parameters was feasible thanks to technical modifications of the equipment. However, it was expected and later shown (see Chapter 4) that such a modification did further enhance the performance only in the order of a small percentage.

Rubberizing of the plasma-treated cord - In Figure 40, the inner construction of the crosshead is shown. The temperature in the crosshead is regulated by a water circuit system which is controlled by the operating system of the extruder. On the right-hand side of the head, the connections of the water hoses are visible. The water is heated up to 95 °C by temperature control unit (TCU) of the extruder and can maintain a temperature of about 89 °C in the crosshead. To get a proper rubber coating of the cord, the rubber compound itself needs a temperature of approximately 110 °C. Therefore, the pre-heating of the crosshead is important to keep the cooldown effect of the rubber that enters the crosshead after being intensively mixed and heated up in the extruder screw as little as possible. The nozzle, which is made of brass, and the die of the crosshead are exchangeable elements, that can be adjusted according to the diameter of the cord. A by-pass is available as well and it is used to regulate the pressure inside the crosshead. The pressure depends on more factors like extruder screw speed, viscosity and the cord pulling speed. Closing the by-pass can significantly increase the pressure inside the head, as all the rubber must leave via the small pinhole exit of the cord. The intention is to build up a pressure level, where not only a coating of the cord is applied, but also a penetration of the rubber into the cord can be achieved. This setup was expected to allow penetration with a combination of extruder screw speed and the variable by-pass opening, which both together give an exact control over the applied pressure.

The product of the plasma line is shown in Figure 41: a plasma treated and rubberized single end cord. In that stage, it is ready to be used for a reinforced composite application providing adhesion after the final vulcanization step. After leaving the crosshead, the rubberized cord will be wound up and separated by a plastic foil to avoid sticking of the uncured rubber.

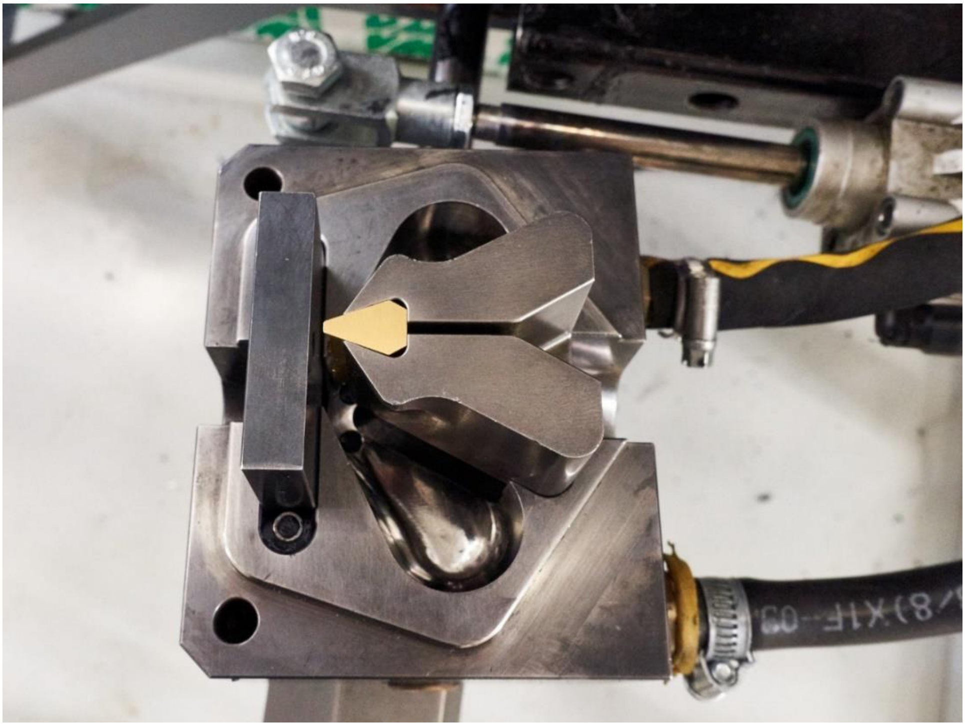


Figure 40: Crosshead of the extruder. The nozzle made from brass is exchangeable as well as the exit die in order to be able to adjust to different cord diameters.

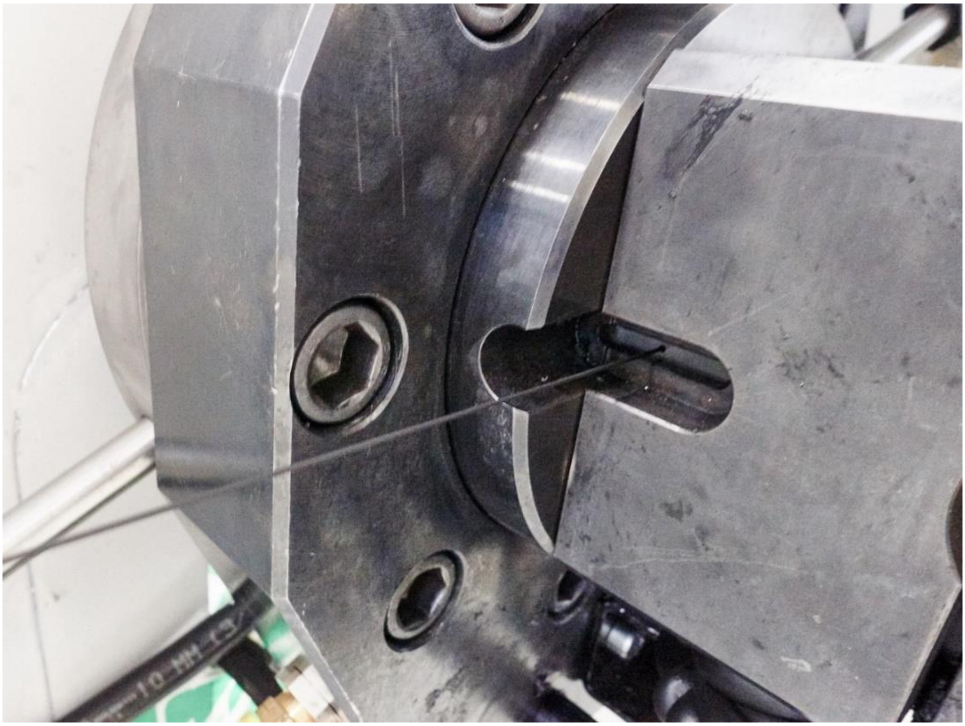


Figure 41: Plasma treated cord exits the crosshead with a rubber coating.

Dipping bath - Another development step was the introduction of a dipping bath, because a better penetration of the rubber into the outer layers of the cord became an important topic. With optimal extruder settings, a certain penetration depth can be reached, see Chapter 5. However, that level might still not match the penetration depth of a RFL coating. An approach to increase the penetration depth was the application of a dipping bath with a polymer solution, which was installed in-between the plasma chamber and the extruder, but within the extended part of the protective atmosphere of the plasma treatment chamber. This measure enabled, that the cord was not exposed to a possible contamination until it gets in touch with the dip. During the dipping, the cord runs through a series of rollers, whose main purpose is the guidance of the cord. One roller pair executes a slight compression on the cord to squeeze out remaining gas located in the center regions of the cord, and to incorporate the dip into the cord. The applied dip consists of dissolved styrene-butadiene-rubber (SBR) in toluene with a concentration of about 3 g SBR in 100 ml solvent. The dip container was designed to be filled with 3 l of dip. The dip can be either a pure version with only the polymer, or a complete rubber compound with all ingredients of the vulcanization system. The dipped cord must be dried before entering the extruder and receiving the final coating by the extruder. Therefore, the cord runs through a drying loop inside the low-pressure cabinet to give the solvent sufficient time to evaporate. A fan, that blows an air stream onto the cord, can be used to enhance the evaporation rate. Alternatively, to this rubber dip with the aim to enhance penetration, a dipping process can be used to soak the cord with a chemical that reacts with the cord surface after plasma treatment. Depending on the reaction, such a dip might require a heat treatment after dipping, which might imply that the rubberizing step cannot be done directly after plasma treatment.

3.3 CONCLUSION AND OUTLOOK

The focus of this project was to promote the adhesion of polymeric cords to rubber making use of a plasma technique. One important requirement of the technology development was the suitability for an industrial process environment. This implied that the plasma-treatment process needed to be compatible with existing lines for tire production, and that the process must run under atmospheric conditions. The plasma line was developed from a basic start setup with only a winding unit and an APPJ plasma device to a sophisticated treatment process with several specialized solutions.

The plasma treatment part of the line consisted of two pairs of APPJ’s. The first APPJ unit was adjusted for a strong, significant etching effect for decontamination of the cord. A second APPJ unit with plasma polymerization abilities was added to the line to deposit chemicals, and therefore new functional groups, on the cord surface. This device was equipped with a chemical supply unit, which delivers the precursors to the plasma nozzle, and can perform plasma polymerization.

A plasma treatment chamber was developed within this part of the study. The tailored layout consisted of a metal plasma modification chamber, as it had to withstand excessive heat under operation conditions. Sealing of the chamber and a slight overpressure of a protective gas to avoid any air entering the chamber and guarantee constant pressure was crucial. The main advantage of the final design of the plasma treatment chamber was the removal of exhaust gases, as they caused problems in an overpressure environment at first instance. Besides, working under a protective environment during and after the plasma treatment is crucial.

The peripheral equipment like a unit for pre-treatment of the cord, the tension control system, the precursor supply unit, the exhaust extraction system, the dipping bath, the crosshead-extruder and the winding unit together with the plasma units constitute the fully operational plasma treatment line. The whole line was elaborated by using a list of initial requirements, and further developed based on experiences gathered by practical use of the plasma line.

However, scaling-up of this line from its current pilot scale to a full sized industrial process will require a significant amount of effort. The current treatment speed of about 10 m/min for a single end cord is too low, in particular if the amount of cord per tire, which is about 1,5 km for each tire, is taken into consideration. The control of the layer thickness of the deposited precursor is highly dependent on the cord speed. When increasing the cord speed to a level that is required for an industrial treatment process, a plasma equipment is necessary that can control the layer thickness independently. Besides, the efficiency of the current setup is rather low due to the single end cord treatment. However, this pilot scale plasma line was built to prove the concept of using plasma treatment for adhesion promotion between rubber and polymeric cords, and that was indeed successful.

CHAPTER 4

Sulfur precursors for plasma treatment as novel options to coat textile cords for rubber adhesion.

This chapter follows an adhesion concept where the cord surface will be modified by plasma treatment. Instead of generating hydroxyl groups on the surface, which is the usual approach for generating reactive groups on a substrate's surface, the alternative concept here is to deposit sulfur moieties. These groups are expected to be able to interact with the sulfur complexes during the vulcanization of the rubber and, thereby form stable chemical bonds between cord and rubber. This concept also has the benefit that the polarity of the cord is decreased and the compatibility with rubber will be enhanced.

4.1 INTRODUCTION

In the present study, a novel route of creating an adhesive layer on a cord surface, which is responsive towards rubber, is explored. The basic concept is the application of plasma polymerization to create such a layer with the help of a precursor, which splits into radicals in the plasma and undergoes a polymerization reaction during the deposition on the cord surface. The process is applicable under atmospheric pressure. As described in the previous chapter, a plasma reactor is the best choice for this modification. The novelty is the use of sulfuric precursors that are applied on polymeric cords in a plasma reactor with protective atmosphere. Usually, the plasma technique is used to enhance the surface energy and polarity to make a surface more reactive for adhesive applications.

Besides the possibility of in-line processing, plasma polymerization at atmospheric pressure has some other advantages over deposition at low pressure. Since the chance that a gas molecule collides with another is significantly higher at atmospheric pressure than in vacuum, energy transfer is more efficient. At vacuum pressure, the monomer molecules are often fragmented, because the plasma species are highly energetic. The lower energy of plasma species at atmospheric pressure results in a better retention of the chemical structure. Furthermore, the higher monomer concentration at atmospheric pressure results in higher deposition speeds.

Several precursors are analyzed in this chapter and compared to each other. Their optimal molecule structure and constitution is evaluated. A possible reaction pattern between the cord and the plasma polymerized layer as well as the rubber is described and a closer look at the actual chemical composition is taken. The effects and improvements of the development steps of the plasma line, which have been described in the previous chapter, are investigated and the influence of significant plasma parameters and their effect on the adhesion are studied.

The chapter starts with the introduction of the plasma precursors used in this study, and the assumed reaction pattern is explained. Furthermore, the tests, analytical methods and procedures are described. The results achieved with rayon and polyester cord are presented. Finally, the chapter ends with a discussion based on the insight gained from this work and a summary.

4.1.1 Sulfur precursors

The use of sulfur containing precursors was considered to be a valid option in order to generate a plasma coating that has the ability to interact with the sulfur accelerator complexes which are formed during the vulcanization of rubber. Several molecules were considered for such an application. Di- and trisulfides may function as a sulfur donor or enhance the chance of interaction with the accelerator complexes. Furthermore, the combination with other functional groups can be of interest, as the molecule may reconfigure itself during the exposure to the plasma or interact with plasma radicals.

Thiophene (C_4H_4S) features a five-membered ring structure of four hydrocarbons and one sulfur atom. Consequently, the molecule: see Figure 42, has two double bonds. The ring structure gives the molecule a certain stability when exposed to plasma. Like pyrrole, thiophene is well known to plasma polymerize under plasma conditions to polythiophene. This polymer can be electrical conductive, however, plasma polymerization doesn’t form polymers with a high stereoregularity. One of the main questions is, if the plasma could activate the thiophene molecule in such a way that the resulting plasma polymer can participate in the vulcanization process.

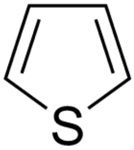


Figure 42: Thiophene molecule

Diallyl disulfide ($C_6H_{10}S_2$) was chosen, because it provides double bonds as well as a disulfide element. However, this molecule doesn’t offer a ring structure which may make it rather vulnerable in the plasma and it is unlikely that it forms a proper polymer. It is more likely, that it might plasma polymerize but not form polymer chains of a proper length and regularity. On the other hand, diallyl disulfide should be relatively easy to activate and therefore, requires a lower energy input. The sulfur-sulfur bond is a particularly weak one with a bond energy of 2.778 eV [78], which implies that it is likely that the molecule will split at this point. The carbon-carbon double bonds are located at the end of the molecule, so they do not contribute to a stable ring-structured molecule like for thiophene. If the molecule splits at the sulfur-sulfur bond in the plasma, it could happen that the double bond and the sulfur radical both react with the cord surface forming a ring structure. Another shortcoming is that diallyl disulfide is in fact condensed garlic liquid, it has a quite repulsive smell at very small concentrations.

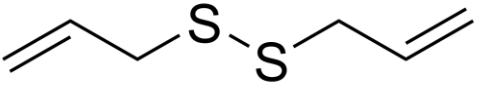


Figure 43: Diallyl disulfide molecule

Dibenzyl disulfide ($C_{14}H_{14}S_2$) is another disulfide that has a similar structure but differs in its functional end groups. Instead of double bonds it features aromatic rings. These rings can get opened by the plasma and undergo radical reactions with the cord surface. A plasma polymerization that forms a certain regular structure like in the case of thiophene is not to expect. However, plasma can create fragments of this molecule which then recombine to structures that have a higher (or lower) molecular weight and are attached to the cord surface. The question is, if those structures have functional groups or allylic positions which can participate during vulcanization. Another question is how the sulfur atoms of the molecule recombine and if they form configurations that can interact with the sulfur accelerator complexes of the rubber to create chemical bonds and consequently adhesion.

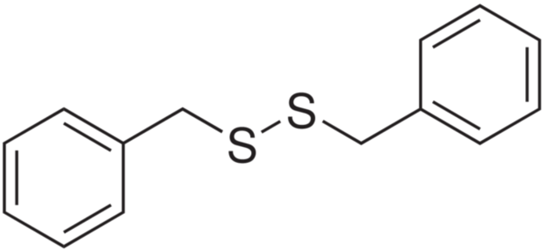


Figure 44: Dibenzyl disulfide

Dimethyl trisulfide ($C_2H_6S_3$) is basically a sulfur chain of three sulfur atoms with a methyl groups attached at each end. A common abbreviation is DMTS. It is indeed missing the double bonds present in the other molecules, though due to the plasma activation of the cord and the molecule itself, a chemical bond of the deposited layer with the cord is possible. Like the diallyl disulfide discussed before, this trisulfide features no ring structure and that makes it vulnerable within the plasma and likely to get atomized. However, the deposition and recombination process might establish sulfur chains within the deposited layer. As there are no double bonds available, the plasma polymerization of the deposited atoms may form a less regularly structured polymer, unlike it is possible with the formerly discussed molecules in this chapter. However, the increased amount of sulfur might create a high reactivity during vulcanization and therefore result in a good adhesion between rubber and reinforcing cord.

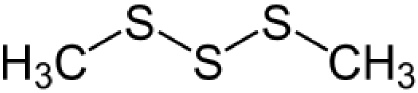


Figure 45: Dimethyl trisulfide

Table 7: Overview of the properties of sulfur precursors [79].

Precursor	***Thiophene***	***Diallyl disulfide***	***Dibenzyl disulfide***	***Dimethyl trisulfide***
Molecular Formula	C_4H_4S	$C_6H_{10}S_2$	$C_{14}H_{14}S_2$	$C_2H_6S_3$
CAS number	110-02-1	2179-57-9	150-60-7	3658-80-8
Molecular weight [g/mol]	84,14	146,28	246,39	126,26
Density [g/cm³]	1,06	1,01	1,30	1,20
Melting point [ºC]	-38	n/a	69-72	-68
Boiling point [ºC]	84	180	210-216	170
Hazard symbol	F, Xn	Xn	Xi	none

Some properties of sulfuric precursors that were introduced on the previous pages are shown in Table 7. They differ from each other in the number of sulfur atoms as well as molecular weight and structure. The idea behind this selection is, that a comparison of these precursors results in a better understanding of the necessary qualities and properties such a molecule must have in order to perform well. In general, a substantial number of possible chemicals can be thought of. However, because of technical reasons with respect to the PAD1 unit, the precursor has to be in a liquid state and its boiling point has to be below 250 ºC, otherwise the precursor cannot be evaporated by the atmospheric pressure plasma jet (APPJ) of the plasma line.

With this variation of precursors it can be deduced, if a certain aspect of a molecule is beneficial for the plasma treatment process. For example, if the number of sulfur atoms plays a role in the coatings' ability to interact with sulfur complexes or if the number of double bonds is a criterion. More than three sulfur atoms in a row in the molecule was considered to be possibly problematic, as the precursor might convert to a lower number of sulfur atoms in its chain by releasing elemental sulfur. This is possible in particular during the evaporation phase and the injection into the plasma. Also, molecules with aromatic rings are difficult to use, as they usually have a high boiling point that is not feasible with the given setup.

An overview of bond energies is given in Table 8. A plasma can atomize a whole molecule which leaves room for recombination in conjunction with surface interactions. That being said, the recombination process of a molecule after it was atomized by plasma is not predictable and happens in a random order.

Table 8: Bond energies of common carbon and sulfur bonds. [80]

Bond	*kJ/mol*	*eV*	*Bond*	*kJ/mol*	*eV*
C-C	345	3.576	C=C	615	6.374
C-O	358	3.710	C=O	708	7.338
C-S	289	2.995	C=S	587	6.084
S-S	268	2.778	S=S	423	4.384
C-N	305	3.161	C=N	616	6.384

4.1.2 Other precursor for comparison

Pyrrole (C_4H_5N) is, just like thiophene, a heterocyclic aromatic organic compound and structured as a five-membered ring [81]. Unlike thiophene, it has a dipole in which the positive end lies on the side of the heteroatom, with a dipole moment of 1.58 D. Pyrrole is prepared industrially by treatment of furan with ammonia in the presence of solid acid catalysts like SiO_2 and Al_2O_3 [82].

Due to its aromatic character, pyrrole is difficult to hydrogenate, does not easily react as a diene in Diels-Alder reactions. Because of its high π-electron density, the characteristic reactions of pyrrole are electrophilic substitutions. Substitution occurs preferentially in the 2-position. The reactions proceed under mild conditions, but must be adapted to the compound's sensitivity towards acids. As an analog to thiophene, pyrrole can polymerize under plasma conditions forming polypyrrole (PPy) [83]. PPy is an insulator, but its oxidized derivatives are good electrical conductors. The conductivity of the material depends on the conditions and reagents used in the oxidation. Conductivities range from 2 to 100 S/cm [84].

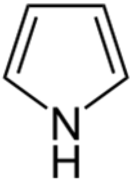


Figure 46: Pyrrole is a heterocyclic aromatic organic compound.

1,3-Butadiene (C_4H_6). The name butadiene generally refers to 1,3-butadiene. The thermodynamically less stable 1,2-butadiene, which has two cumulated double bonds, has only minor industrial importance. The 1,3 isomer is economically the most important unsaturated C_4 hydrocarbon [85]. Butadiene has two conjugated double bonds and therefore can take part in numerous reactions, which include 1,2- and 1,4-additions with itself (polymerization) and other reagents, linear dimerization and trimerization, and ring formation. Non-stabilized or insufficiently stabilized butadiene forms explosive peroxides with atmospheric oxygen. Butadiene is sparingly soluble in water, soluble in methanol and ethanol, and very soluble in higher-boiling polar solvents, e.g., methylpyrrolidone.

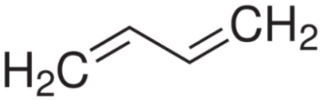


Figure 47: 1,3-butadiene is a hydrocarbon with two double bonds.

Tetrahydrothiophene (C_4H_8S) is the saturated equivalent of thiophene. It therefore consists as well of a five-membered ring containing four carbon atoms and a sulfur atom. It is a volatile, colorless liquid with an intensely unpleasant odor. Together with its unsaturated analog and pyrrole it can be used to study the effect of plasma treatment on these ring-structured molecules.

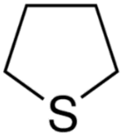


Figure 48: Tetrahydrothiophene

4.1.3 Plasma polymerization of thiophene and pyrrole

In general, both chemicals can polymerize. The polymerization reaction can be initiated with different techniques; one of them is plasma. The mechanism behind this is, that the plasma accelerates electrons of the ionized gas which undergo a high number of collisions because of the atmospheric conditions at which the plasma is ignited. These excited electrons also collide with the injected precursor molecules, which are the monomers like thiophene or pyrrole. In case of an inelastic collision, in which one of the ring electrons is ejected, for example a radicalized thiophene cation originates. This radical can either form a di-cation with a second radical cation or react with another thiophene monomer starting a radical polymerization. These reaction patterns are shown in Figure 49, where the initiation was an electrochemical one [86]. The polymerization conditions in the plasma are rather poor, as there is only a limited amount of monomer injected which also limits the possibilities to form a polymer of a reasonable molecular weight. The quality of a plasma polymerized polythiophene (PT) layer is affected by several factors, such as plasma strength, frequency, cycle time, gas type, treatment time and precursor flow-rate. Two other important but interrelated factors are the structure of the monomer and the applied potential. The potential required to oxidize the monomer depends upon the electron density in the thiophene ring π-electron system. Electron-donating groups lower the oxidation potential, while electron-withdrawing groups increase the oxidation potential.

Usually no specific structure results from polymerization in a straightforward manner under plasma conditions, as significant fragmentation and rearrangement of atoms in the original starting material occurs frequently. However, the structure of the monomers largely determine the fragmentation pattern that occurs in the plasma. It is a random process and predictions are not reliable [87]. The ring structures of thiophene and pyrrole avoid the entire fragmentation that occurs with other precursors. Therefore, the previously described reaction pattern can take place and form either polythiophene or polypyrrole (PPy). This is in a certain contrast of using a desired functional group in conjunction with double bonds which easily create radicals under plasma conditions or a ring structure that opens up during the plasma treatment [88], which is a good approach to create plasma polymerized structures on a substrate surface that are suitable for the desired task.

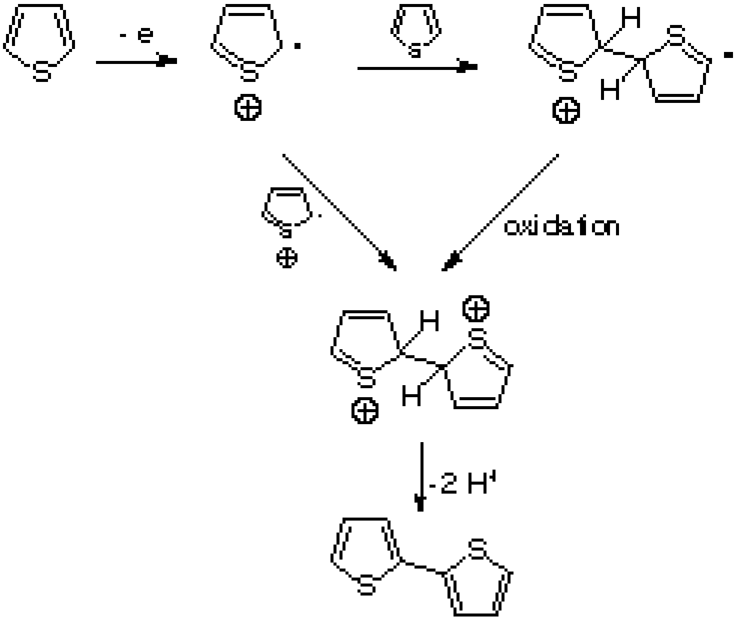


Figure 49: Electrochemical polymerization pattern of polythiophene [86].

The plasma treatment of the cord was performed under nitrogen conditions using the new concept of a plasma treatment chamber (see Chapter 3). In first place, a decontamination step was applied, while in second place the actual plasma coating with a sulfur precursor was performed. Inside both chambers, an overpressure of about 0.2 bar was established via controlling the exhaust streams with external valves. In fact, the suction was reduced until a slight overpressure inside the chamber was established and the desired nitrogen protective atmosphere was created. The presence of a nitrogen protective gas atmosphere can be checked by the visual appearance of the plasma flame. Only in a nitrogen atmosphere, a strong plasma glow effect occurs, like it was shown in Chapter 3. While oxygen is still present in the chamber, this glow cannot be established, which makes it a clear and useful indicator.

4.2 EXPERIMENTAL

4.2.1 H-pullout test

This test method measures adhesion of reinforcing cords bonded to rubber compounds, and is applicable to all textile cords from both natural and manmade fibers. However, it is not valid for steel cords. The method is documented in the ASTM standard D4776M-10 [89].

The test specimen is made in a way, that a cord specimen is sandwiched between two layers of rubber compound at each end of the specimen. Therefore, a single specimen is resembling the shape of an “H”, which is the origin of the name of the test. One mold produces 30 specimens per batch, as it has ten cavities for rubber stripes and six rectangular directed slots for cord: Figure 50. The pre-heated mold gets equipped with rubber and cord material. It then is placed in the vulcanization press and the rubber is cured at a specified temperature and pressure. The test specimen sandwich is afterwards cut to create a H-test specimen consisting of a single cord with each end embedded in the center of a tab end of the rubber test block. The test specimen is placed in the grips of the tensile tester, and then the grips are separated. The maximum force obtained is the H-test adhesion force [89].

This test method is primarily used to evaluate tire cords, using a suitable tire cord adhesive and an appropriate rubber compound. The test method can also be used to evaluate tire cord adhesives or the process of adhesive reaction on the cord using one consistent form of tire cord and rubber compound. This test method may be used to evaluate cords in industrial hose and belting products and other cord reinforced rubber products.

H-pullout tests must be performed in standard atmosphere for testing tire cords, which is 24 °C and 55 % relative humidity. A tensile tester needs to be prepared with dedicated test grips. In fact, the grips have a non-mechanical design; they simply match the rubber shape of the specimens with a hole for the cord. An axial alignment of both grips is a necessity. The gage distance between the grips should be set to 1.5 mm and the crosshead speed to 125 mm/min. A H-test adhesion specimen is inserted in the clamps, having one leg of the “H” in the upper clamp, and the other leg in the lower grip.

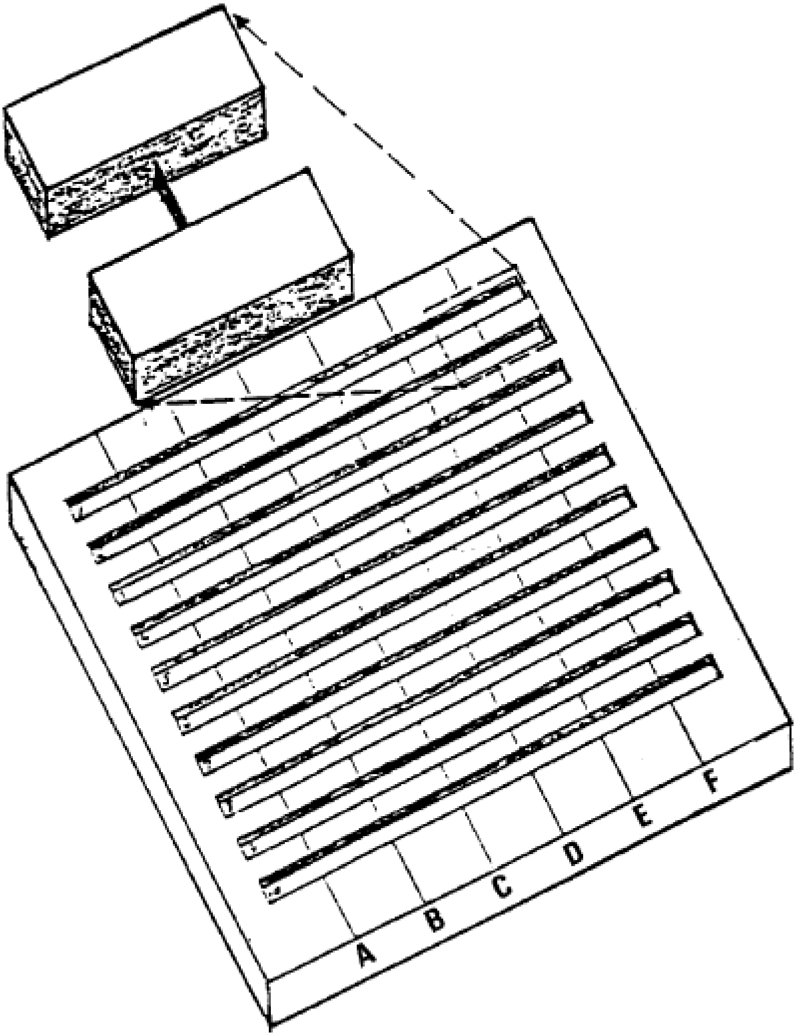
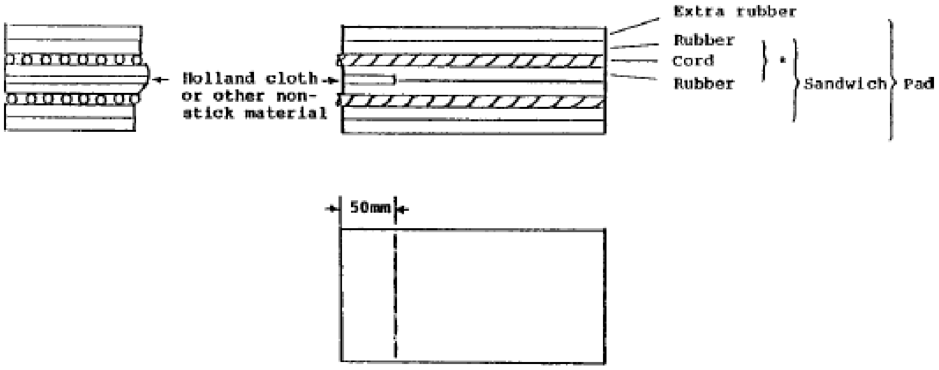


Figure 50: Drawing of an H-pullout specimen (top) and the responding mold [89].

Activation of the crosshead starts the measurement, where first a pre-force of 0,5 N is slowly approached and then the data recording starts and the full test speed is applied. The data recording is terminated when the specimen fails and the crosshead movement stops. The test is repeated with similar samples until a statistical relevant number of test specimens has been tested; in the present work, each batch was tested with 5 test specimens.

4.2.2 Strap Peel Adhesion Force (SPAF) test

The SPAF test is the standard test method for strap peel adhesion of reinforcing cords or fabrics to rubber compounds as defined in ASTM D 4393 [90]. The test specimens for this type of adhesion measurement are made of a composite with a structure that is shown in Figure 51. The composite is a sandwich of three rubber layers and in between two cord layers, where the cords are placed parallel to each other in such a way that they form a flat sheet. The test specimens are 20 mm in width and 110 mm in length. The long side of the test specimen must be parallel to the mill direction. The vulcanization conditions are t_{90} + 6 min at a cure temperature of 160 °C in a dedicated mold.



* One layer of weftless fabric pre-assembled on a rotatable drum in the example of pad building from a single cord.

Figure 51: SPAF composite construction [90].

The test is performed with a tensile testing machine, which has to fulfill the requirements of ISO 5893, with an accuracy of force measurement complying to class 2 and a 10 kN load cell. The grippers for holding the test specimen in the testing machine during the measurement correspond to ASTM D 413. The measurements are performed with an initial gripper distance of 20 mm, the transfer rate of the gripper is 100 mm/min. The force is measured as a function of peel distance. However, the primary information gathered by this test is the degree of rubber coverage, which is expressed as a percentage value judged by the operator. It can be given a value of 100 % coverage, which is equivalent to a failure entirely within the rubber phase in between the cord layers. If the failure is also partly at the interface, the coverage value can be judged stepwise with 90, 80, 70, 50 or 30 % of coverage. The SPAF tests in this thesis have been performed in the laboratories of Apollo Tyre Global R&D B.V. in Enschede, the Netherlands. The tensile tester used was a Zwick Z100.

4.2.3 X-Ray Photoelectron Spectroscopy (XPS)

XPS is a tool for the chemical analysis of a surface layer suitable for any solid substrate. It is also known as electron spectroscopy for chemical analysis (ESCA). This technique is nowadays the standard tool of almost all surface analysis labs worldwide, whether academic or industrial. With XPS it is possible to determine the elemental composition of the very outer atomic layers of a solid and, therefore, to do a characterization of the top 1-10 nm of a solid sample. The information received from a XPS measurement is heavily limited for an unexperienced researcher, as it requires detailed analysis of the collected data. One limitation of the XPS technique is, that it is not able to detect hydrogen and helium within solids. The reason for this limitation is that their photoelectron cross sections are below XPS detection limits [91]. XPS analysis is optimized toward core electrons and is not highly sensitive to valence electrons, while hydrogen and helium only have valence electrons which makes them undetectable by XPS.

These are XPS core abilities:

- Identify and quantify the elemental composition of the outer 10 nm or less of any solid surface. All elements from Li to U are detectable;
- Reveal the chemical environment in which the particular element exists;
- High sensitivity; can detect minimum concentrations of 0.1 atomic %;
- Surface resolution is in the range of 1 – 10 nm;
- Obtain the above information with relative ease and minimal sample preparation.

There are three more methods, which can do similar analysis. Two of them are related to XPS. These are the Ultraviolet Photoelectron Spectroscopy (UPS), which is basically an extension of XPS that measures the valence band photoelectrons, and Auger Electron Spectroscopy (AES), which is sensitive to the same elements and has an improved spatial resolution. However, this method is less sensitive than XPS. Besides, a Scanning Electron Microscope (SEM) with an additional Energy Dispersive X-Ray analyzer (EDX) has similar capabilities. The main difference here is, that the SEM EDX scans the elements up to 1µm or more below the surface. This difference in depth is important since nearly all the surface chemistry is dictated by the chemical composition, speciation, and/or electronic structure present over the few outer atomic layers of the respective solid [91]. These can differ substantially from those noted 1 nm or more below the surface. A surface film of 1 nm equates to three to four atomic layers. Thus, the examination of aluminum foil via EDX reveals spectra heavily dominated by aluminum peaks. This would not reveal the presence of a surface oxide [91].

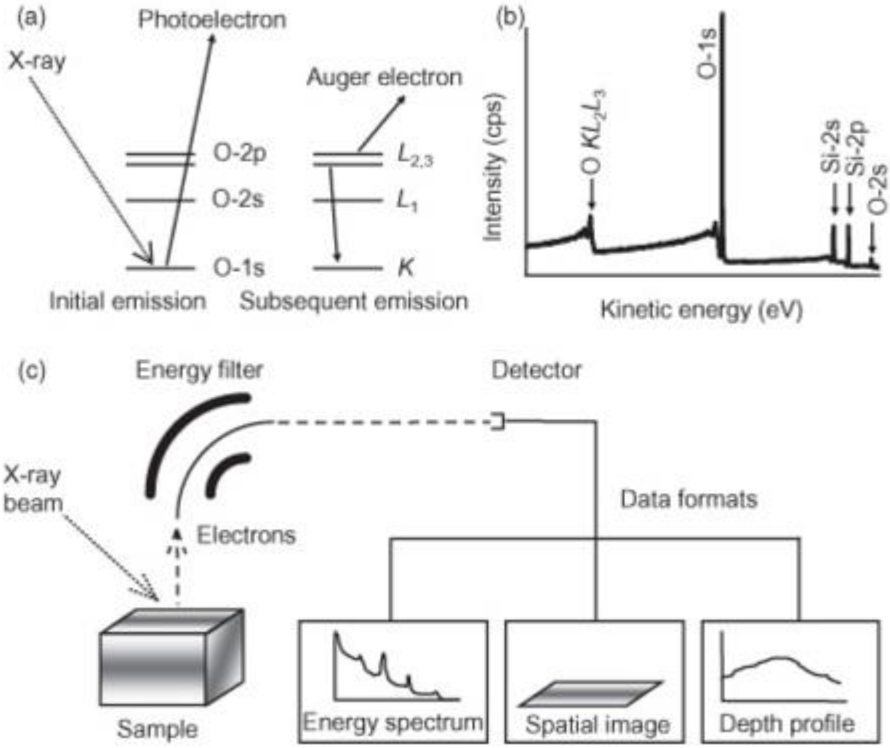


Figure 52: a) Sketch of how a X-ray beam causes initial and subsequent emissions, that can be detected; b) a typical spectra received from a XPS measurement; c) scheme that shows the basic principle of XPS technique [91].

The basic aspects and physical principles that underlay XPS are shown in Figure 52. A typical XPS spectrum (Figure 52b) is a plot of the intensity (cps) versus the kinetic energy (eV) of the electrons detected. Each element that is registered by the detector of the XPS produces a characteristic set of XPS peaks at characteristic energy levels. That makes it possible to directly identify each element, as these peaks correspond to the electron configuration (1s, 2s, 2p, etc.) of the electrons within the atoms.

The XPS measurements used for the present work were performed with a Quantera SXM (scanning XPS microprobe) from Physical Electronics equipped with an Al Kα X-ray, which is monochromatic at 1486.6 eV. The working pressure was 2 x 10^{-8} torr and the remaining gas was argon for neutralization. The analysis was done with Compass for XPS control and Multipak v.9.4.0.7 for data reduction. Fitting of spectra was done after shifting of the measured spectra with respect to the known reference binding energies. The samples were taken directly from the plasma treatment process, where they were put in a plastic bag protected by a nitrogen atmosphere and directly transported to the XPS lab. The samples were cut to a suitable size for the XPS vacuum chamber and attached to a sample holder. The samples holder was placed immediately into the XPS and kept under vacuum until the measurement was performed.

4.2.4 Stereo Microscope

A stereo microscope from Leica of the type MZ 125 was used to analyze the plasma treated samples optically. The stereo microscope uses two separate optical paths with two objectives and two eyepieces to provide slightly different viewing angles to the left and right eyes [92]. In this way, it produces a three-dimensional visualization of the examined specimen. In microscopy, depth of field is often seen as an empirical parameter. In practice, it is determined by the correlation between numerical aperture, resolution and magnification. For the best possible visual impression, the adjustment facilities of modern microscopes produce an optimum balance between depth of field and resolution – two parameters which in theory are inversely correlated [93]. The stereo microscope has a useful magnification up to 100X. To capture images, a digital camera, a Leica DFC 240 with 3 megapixels, was used and the images were edited, saved and organized with the Leica LAS 3.8 software. As samples, H-pullout specimens after testing were taken. They were cut either perpendicular to the cord direction or, if the cord was pulled out from that sample part, cut parallel to the cord direction to monitor the failure interface. Those specimen parts have been reduced in size to an effective dimension of roughly 5 x 5 x 5 mm. Modeling clay has been applied to secure the specimen when placed under the microscope.

4.2.5 Laser Scanning Confocal Microscope (LSCM)

A laser scanning confocal microscope (LSCM) has several advantages over conventional optical microscopy:

- Suitable for high resolution imaging;
- Controllable depth of field, comparable to SEM;
- Elimination or reduction of image degrading out-of-focus information;
- Ability to collect serial optical sections from thick specimens;
- Several analysis functions, including profile and roughness;
- 18,000x magnification with Z-axis resolution of 1 nm;
- Measures thickness and uniformity of clear layers.

The key element of the confocal approach is the use of spatial filtering to eliminate out-of-focus light or glare in specimens whose thickness exceeds the immediate plane focus. This contrasts with a conventional microscope, where the entire specimen is engulfed in light. Confocal technology is one of the most important advanced techniques in optical microscopy and takes advantage of modern computer technology. It was initially mainly used in biological research, living cells etc., but is nowadays applied in several research fields.

Image formation in a confocal microscope is fundamentally different. Illumination is achieved by scanning one or more focused beams of light, usually from a laser, across the specimen [94]. This point of illumination is brought to focus in the specimen by the objective lens, and laterally scanned using some form of scanning device under computer control. The sequences of points of light from the specimen are detected by a photomultiplier tube (PMT) through a pinhole (or in some cases, a slit), and the output from the PMT is built into an image and displayed by the computer.

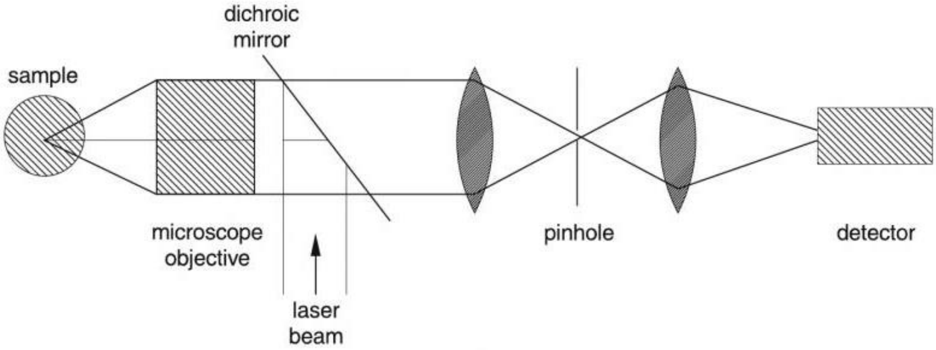


Figure 53: General setup of a laser scanning microscope [95].

In the present thesis, a laser scanning microscope type VK 9700 from Keyence was used. As samples, used H-pullout specimens after testing were taken, similar in preparation as for the stereo microscope.

4.3 RESULTS

4.3.1 Rayon

The results discussed in this chapter reflect two development streams. One is related to the enhancement achieved in the design and layout as well as technical upgrades of the plasma line, which were described in the previous chapter. Improvements in the results due to this kind of upgrades will be discussed. The other development stream reflects the treatment settings, the use of precursors and enhancements due to the knowledge gained during this project. It involves alternating steps along both streams to step-by step achieve most optimal results. In this study, untreated polymeric cords made of rayon and polyester were used. The rayon cord used in this thesis is a type 610F Super 2 1840 dtex f1000 x2, which was kindly supplied by Cordenka GmbH & Co. KG, Obernburg, Germany.

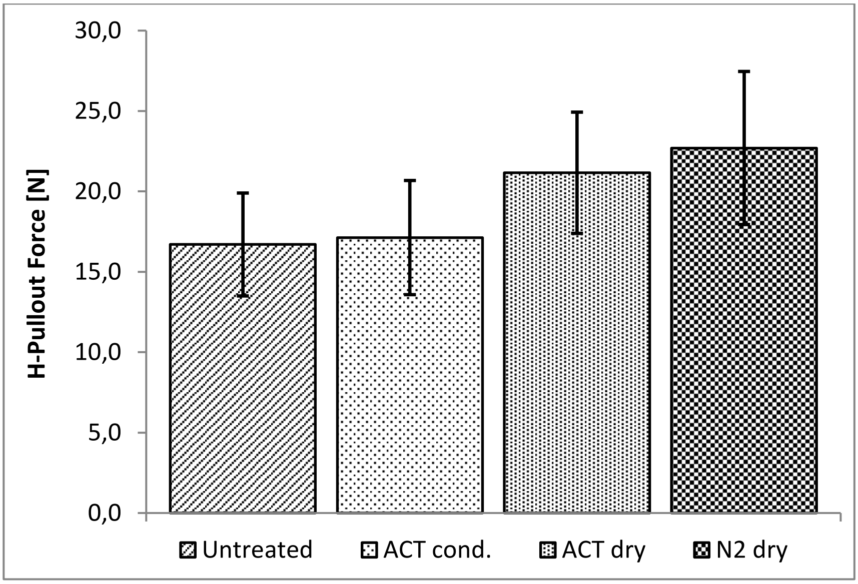


Figure 54: H-Pullout values of untreated, acetone washed (conditioned and dried) and dried nitrogen plasma treated Rayon cord.

Process development/Cord pre-cleaning - A reinforcing cord without the typical final coating, which is in fact an adhesion dip, has an oily finish on its surface, which potentially affects further treatment steps. Therefore, the cord was washed in an acetone solution to remove any remaining finishing substances. After washing, the cord was dried under normal atmospheric conditions as well as in an oven. These cleaned cords were compared to an untreated, so to speak contaminated, cord and a plasma treated cord, where the ionization gas was nitrogen. The results of the H-test, thus the adhesion force to rubber, are shown in FFigure 54. Clearly, the untreated rayon cord and the acetone cleaned but not oven-dried cord (ACT cond.) exhibit lower adhesion forces. The acetone-washed and oven-dried cord as well as the plasma-treated cord show a trend to gain adhesion over the untreated cord and non-dried cords. Interestingly, removing the residual moisture from rayon, which is approximately 6 wt% according to the supplier, has a stronger effect on adhesion than a possible contamination of the cord with oily substances during production. However, it is to note, that the tendency of gaining in H-pullout force remains within the error of the measurement. More important is the fact, that the plasma treatment with a Plasmatreat FG1001 generator in the initial stage of the plasma line was not able to enhance the adhesion with a nitrogen plasma treatment significantly. This contrasts with other results [96], where a nitrogen plasma could enhance the adhesion substantially.

Plasma generator settings - It turned out that the FG1001 generator was not powerful enough for the operation with nitrogen as plasma gas to gain the desired effect, as the older circuit board design was made for operations with compressed air only. A maintenance of the generator confirmed that an update was not feasible. The FG1001 system was considered not to be suitable as main generator for the further use in this project.

Therefore, a modern Plasmatreat FG5001 generator with plasma coating ability, called “Plasma Plus” was purchased as main plasma treatment unit (PU), while the FG1001 was used as cleaning unit (CU) for the pre-treatment or decontamination of the cord. A more detailed description of the setup is given in Chapter 3. Both units were installed under atmospheric conditions in a cabinet with suction unit.

To determine, which plasma settings have a significant effect on the cord treatment process, a Design of Experiments (DoE) plan was made. The FG5001 generator allows the configuration of several parameters. These are mainly parameters concerning the generator power itself, the gas pressure and the flow-rates of the precursor, which is a chemical that is injected into the plasma in evaporated state for plasma coating purposes, and the ionization as well as the carrier gases.

Experience had shown that the gas flow-rates are supposed to have minor effects on the plasma properties and, therefore, could be kept constant for the DoE plan. The factors with a major effect (see **Table 9**) on the treatment process were expected to be the voltage setting (in percentage) of the generator, the frequency in kHz of the excitation process and the cycle time, which determines how long the excitation is activated per cycle. Additionally, the flow-rate of the precursor was considered to have a significant effect on the process. However, the precursor itself was kept constant, and with pyrrole a precursor was chosen, that is known for its ability to plasma polymerize [97].

Table 9: The selected plasma parameters for the DoE trials.

Factor	Type	-	+	CP
A	Voltage [%]	85	100	92,5
B	Frequency [kHz]	19	25	22
C	Cycle time [%]	50	100	75
D	Flow-Rate [g/h]	20	100	60

The following plasma settings were constant during the DoE trials:

primary pressure [mbar]:	1000
flow-rate ionization gas [L/h]:	2074
flow-rate carrier gas [L/h]:	271
temperature evaporator [°C]:	133

All gas related values were kept at the original settings of the system set by the supplier. The temperature of the evaporator for the precursor were set to a temperature above the boiling point of pyrrole, which is 129 °C.

Table 10: The performed trials and the corresponding results as H-pullout forces in [N].

#	A	B	C	D	Answer
1	-	-	-	-	9,3
2	+	-	-	-	10,4
3*	-	+	-	-	-
4*	+	+	-	-	-
5	-	-	+	-	9,8
6	+	-	+	-	9,5

7*	-	+	+	-	-
8	+	+	+	-	10,1
9	-	-	-	+	9,5
10	+	-	-	+	9,3
11*	-	+	-	+	-
12*	+	+	-	+	-
13	-	-	+	+	9,8
14	+	-	+	+	10,9
15	-	+	+	+	11,2
16	+	+	+	+	11,6
CP	0	0	0	0	11,1

*** These rows are parameter settings that did not allow plasma ignition.**

The performed trials, which consequently consist of 16 trials plus a center point (CP) test, are documented in Table 10. The answer column reflects the measured H-pullout force values of each sample. A few factor combinations turned out not to be feasible, because the generator was not able to ignite the plasma under these circumstances.

Clearly, the values are very low and do not match the expectations. The adhesion is even lower than the one documented for the untreated cord in FFigure 54. Independently, from the combination of factors the results are not satisfactory. The fact that the values are all low, supports the hypothesis that another factor is responsible for the poor results. That might be the precursor itself, which might not have formed moieties during the plasma coating which can interact with the sulfur complexes during vulcanization. In this case, the coating would make the cord even more inert, what subsequently prevented any development of adhesive forces between coating and rubber. Another possible explanation is that the freshly plasma treated cord surface reacted with the surrounding air in a way that the top-layer got oxidized, which made the surface polar and blocked the interaction between coating and rubber.

XPS analysis - To better understand what happened to the cord surface after the plasma coating, four samples with either strong or weak plasma settings and either high or low flow-rates were chosen to be analyzed by XPS.

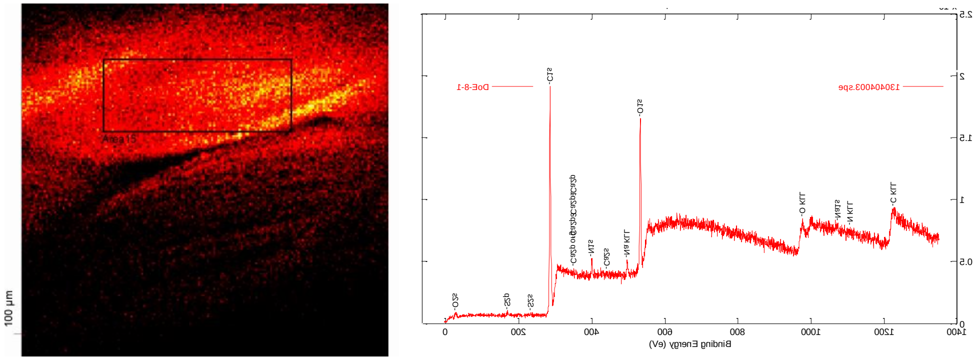


Figure 55: Left: measurement area of the XPS; right: corresponding spectrum of sample DoE-8.

The left-hand side of Figure 55 shows the measurement area of the XPS chosen by the operator. Visible are the two plies of the cord, where one ply is the brighter area on the top and the other one is the darker spot below. On the right-hand side is the corresponding spectrum of the sample shown, which is a plot of the peak intensity over the binding energy (eV).

Table 11: Results of the XPS measurements for the four DoE samples and an untreated reference.

Sample	Description	C	N	O	Na	S	Ca
Reference	No treatment	80.23	1.06	17.36	0.46	0.40	0.48
DoE-16	Strong plasma High flow rate	81.26	1.78	16.25	0.39	0.14	0.18
DoE-8	Strong plasma Low flow rate	80.13	2.16	16.67	0.67	0.22	0.15
DoE-9	Weak plasma High flow rate	80.01	2.18	17.24	0.20	0.28	0.09
Doe-1	Weak plasma Low flow rate	80.53	1.97	16.91	0.37	0.37	0.02

In Table 11 the results are listed, which lead to the conclusion that the differences are so small, that the question may be asked if there is a significant amount of coating deposited. There is a change in nitrogen (N) and calcium (Ca) content visible for the DoE samples, which is an indication that a coating layer is indeed deposited. But as the spectra of all samples are very similar, the XPS apparently still detects the actual rayon surface, which speaks against a continuous well covered coating. DoE-16, the sample with the most intense plasma setting, has an increased carbon (C) content while having the lowest oxygen (O) content, but as there was only one measurement per sample, this has to be taken with caution. Overall, the results do not allow for a confident judgement about what kind of change happened due to the plasma treatment of the surface.

Influence of precursors - Figure 56 shows a comparison of different precursors applied under identical treatment conditions. Only the evaporator temperature setting was adapted to the corresponding precursor evaporation temperature. The precursors were compared, because the DoE trials raised the question if the missing effect of different plasma parameters was caused by inefficiency of pyrrole as precursor. It is clearly seen that thiophene showed the best adhesion values. However, these results are not significantly better than the ones of the DoE trials. Therefore, it can be concluded that the unsatisfying H-pullout forces given in Table 4 are not caused by the type of precursor, and neither by the plasma settings. The conclusion from these results is, that the interactions with the surrounding air after the actual plasma treatment can cause a passivation of the cord surface, which causes the low adhesion values.

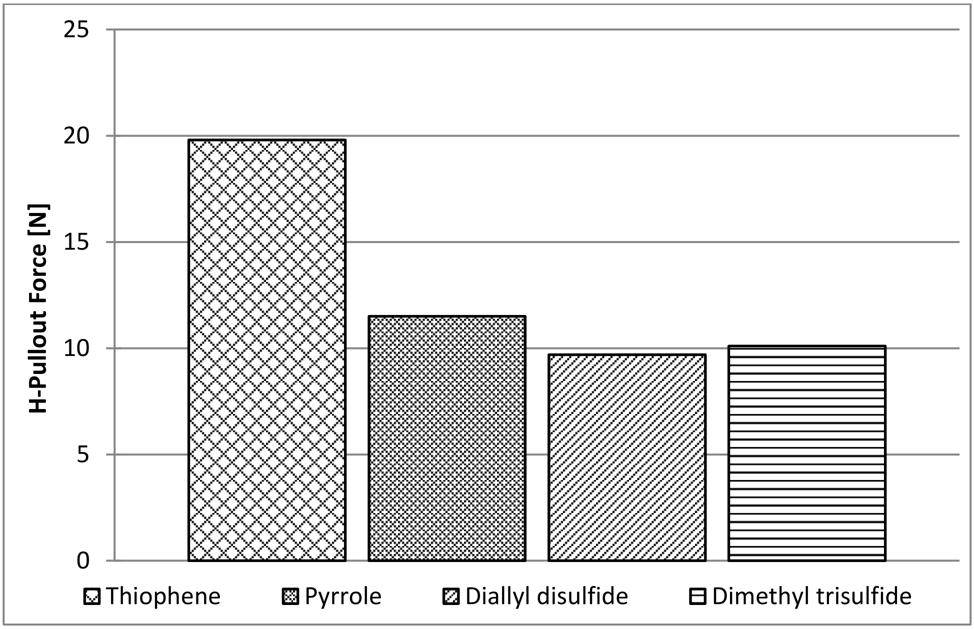


Figure 56: Comparison of thiophene with pyrrole and a disulfide as well as a trisulfide as precursor.

This observation is not easy to prove. It requires a protective atmosphere that prevents any interaction of the cord until the next reaction step is happening. The procedure to achieve this that was developed in this project as described in detail in Chapter 3. In short, a plasma treatment chamber was built that uses a slight overpressure of an inert gas to avoid contamination by air molecules. Such a solution greatly enhances the control over the treatment conditions during the plasma treatment process. To further protect the cord after the plasma treatment, another step was added to the process: The cord remains in an extension of the plasma reactor where the protective atmosphere is maintained until the cord enters directly into the crosshead of the extruder, where it gets immediately rubberized and protected. The initial reactor chamber was built with the intention to prove this concept. However, this chamber was not temperature stable over longer treatment times. To ensure that the treatment conditions were always under control, a solid metal construction was necessary. While this delayed the project for several months, it was a mandatory decision.

Most commonly hydroxyl groups are used to create functional groups on a surface, which are reactive towards alkoxy or epoxy groups as well as acids. The attempt was different here: oxygen was purposely avoided, and the reactive moieties were directly created by the plasma polymerization of the precursors.

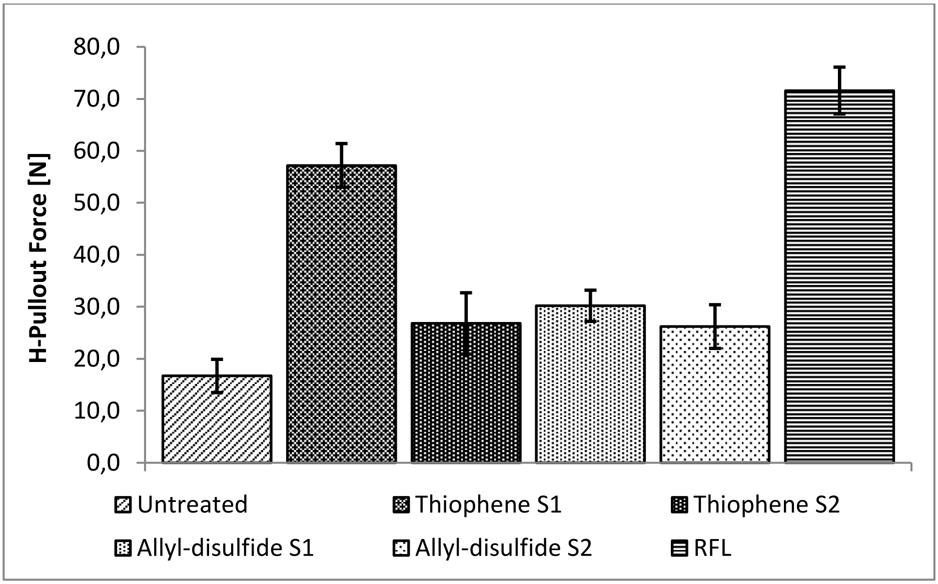


Figure 57: H-Pullout forces measured after the introduction of a protective atmosphere concept.

From Figure 57 it can be deduced, that the concept of a protective nitrogen atmosphere with immediate rubberization afterwards enhanced the adhesion force significantly. Again, thiophene as precursor exhibits its clear potential, here in a comparison with diallyl disulfide. The adhesion of rayon with thiophene as precursor improved by a factor of three. In this case, the new plasma reactor was used. The figure also illustrates a strong influence of the plasma settings, as experiments were done with full generator power (index S1) and reduced generator power (index S2). In both cases, the full power setting S1 enhanced the adhesion, in case of thiophene it had a significant effect. Besides the cords treated with the two precursors, also the untreated rayon and a RFL treated cord (from Cordenka GmbH) were compared. The RFL adhesion is superior, but the results with thiophene are most encouraging and coming close.

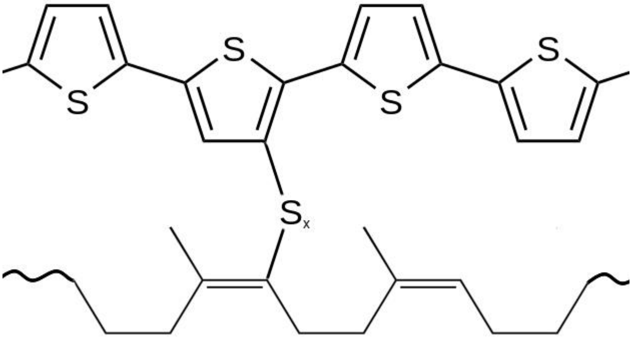


Figure 58: Possible reaction scheme between polythiophene and rubber during vulcanization.

The strong difference caused by the plasma settings for thiophene imply, that chemical bonds are responsible for the good adhesion values in case of the S1 setting. For both settings, the precursor flow-rate is similar, therefore the difference of both variants is the efficiency of deposition. Apparently, the S1 type deposition allows, caused by the stronger plasma power, a more efficient plasma polymerization of thiophene. The polymeric layer formed under these plasma conditions can react with sulfur complexes during the vulcanization progress. A reaction scheme is proposed in Figure 58. From the precursors that have been tested, only thiophene enhanced the adhesion significantly. A look at its molecular structure shows three features, which in synergy explain the enhancement. These properties are:

- a five-membered ring-structure of the molecule;
- two double bonds;
- one sulfur atom.

How important the ring-structure of thiophene is, which keeps the precursor relatively stable in the plasma, was already demonstrated by the comparison with diallyl disulfide. That molecule has double bonds as well as sulfur atoms, but lacks the ring-structure. Clearly, it exhibits less adhesion as seen in Figure 18. An explanation for the lower adhesion is likely, that the molecule gets atomized in the plasma and, therefore, is not able to polymerize in a comparable way as thiophene does.

To learn more about the relevance of the double bonds within the molecule, a comparison of thiophene with tetrahydro-thiophene was done. The latter one is the saturated analog of thiophene and therefore the a suitable candidate to determine the influence which the double bonds of thiophene have on the adhesion.

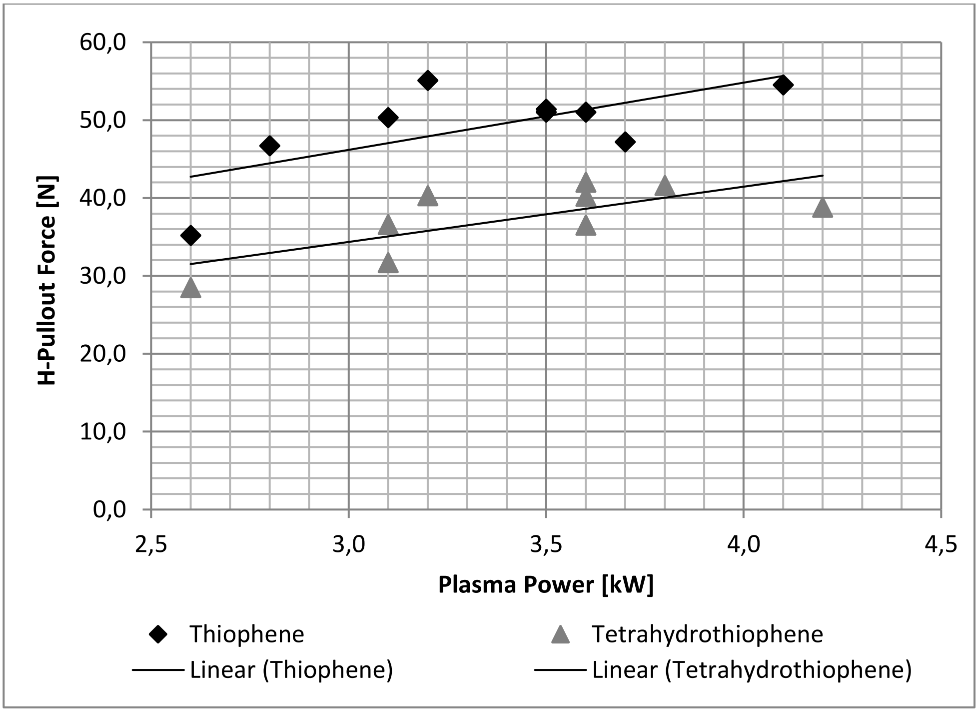


Figure 59: Trend of adhesion with increasing plasma power.

Increased plasma generation power - In Figure 59, the trend of adhesion over increasing plasma power is plotted for the two precursors in comparison. At the lowest plasma power setting, which is 2,6 kW, both precursors show a similar performance. There is almost none improvement over the untreated cord. When the plasma power is increased, both precursors benefit from the more intense plasma. The adhesion values of thiophene increase by about 20 N when the plasma power is raised to 3,2 kW. The effect on the tetrahydrothiophene is similar, but less strong. The double bonds are therefore a clear factor for adhesion promotion, as they are beneficial for the plasma polymerization process which probably leads to a better polymer coating. A higher plasma power than 3.2 kW does not further enhance the H-pullout forces, but there is no negative effect as well. The results show, that a plasma power of more than 3 kW is required for an improved performance. T, the values have a certain fluctuation, which is an indication that the plasma treatment process is still not entirely under control.

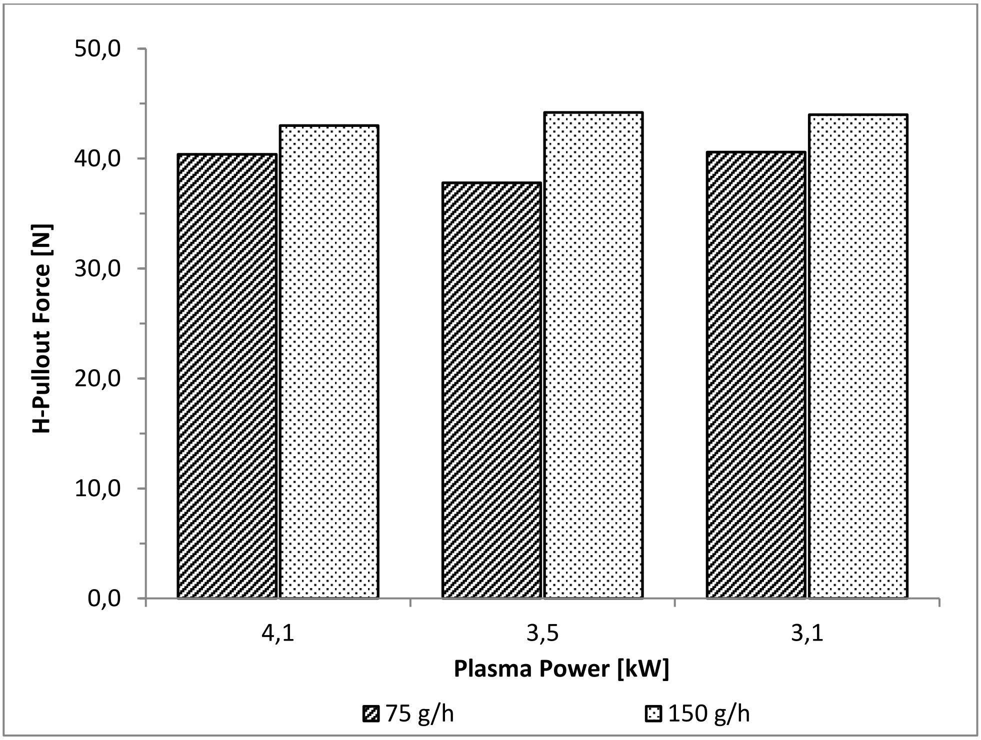


Figure 60: Influence of the precursor flow rate in g/h at different plasma power settings.

Further tests with thiophene and different flow-rates as well as generator settings: Figure 60, were performed to determine where the optimum of these parameters is. While a certain benefit of a higher flow-rate is detectable, the increase of plasma power had no effect above the previously observed 3.1 kW. The tests were performed in one run without stopping the plasma line. One sample was taken and while the line continued running, the next generator flow-rate was set and then the next sample was taken once the line was stabilized. This procedure was the most effective way to run the plasma treatment line. The absolute values were lower than before when similar settings were applied. Apparently, the effect of plasma treatment reduces over time.

Effect of exhaust gasses - A plausible reason for this phenomenon is, that over time more and more exhaust gasses from the plasma treatment process are congested in the plasma reactor. This is caused by the slight overpressure used to create an inert atmosphere. While at the beginning of the treatment a nitrogen filled reactor chamber is present, the off-gasses accumulate and pollute the chamber atmosphere. The conditions in the chamber therefore change with the ongoing treatment. To verify this hypothesis, a dedicated test was done, were no changes to the settings over a period of time were done. Every two minutes a sample was taken, which was afterwards tested with H-pullout tests.

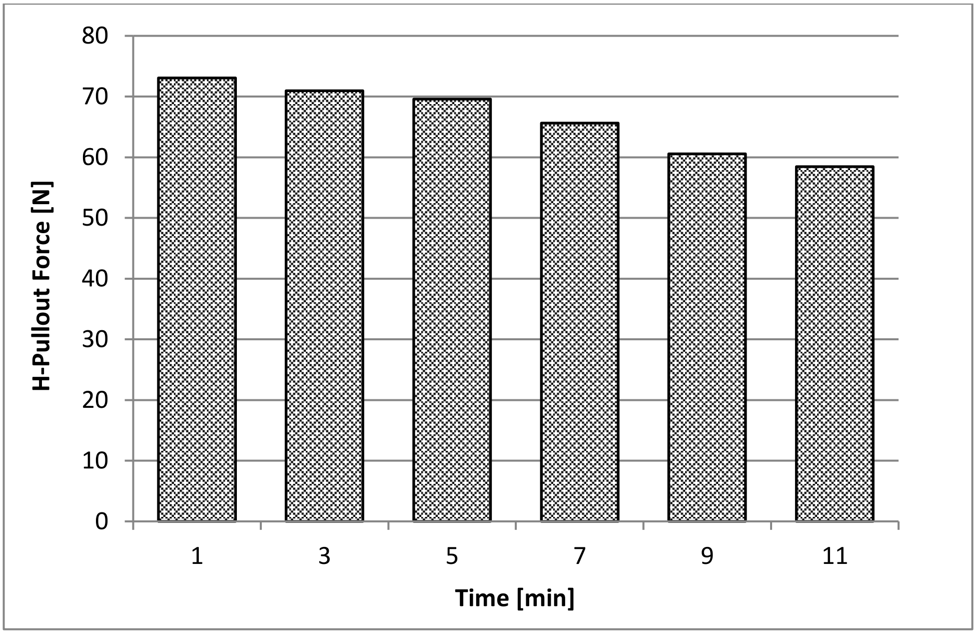


Figure 61: Decrease in H-pullout force during a long-lasting plasma treatment.

The results are shown in Figure 61: Clearly, a negative effect is measurable over time. After 5 minutes of constant treatment a significant decrease is observed. While it was not possible to entirely avoid the effect of contamination by exhaust products of the plasma treatment, as the slight overpressure during treatment is necessary, two solutions were integrated to the plasma reactor to avoid this contamination. The main measure to reduce this effect was to relocate the position of the suction point. It was initially positioned at the end of the treatment chamber close to the extruder (see Chapter 3, Figure 9 at the end of the exhaust pipe). The new position was located close to the actual plasma jets. Behind the new suction point, additional nitrogen was injected into the chamber to avoid a contamination just after the treatment.

Effect of Sulphur-level in precursors - After the problem with the long-time instability of the process was solved, the focus returned to the precursor properties. Two effects have been already analyzed, that were the ring-structure of the molecule and the presence of double bonds. The third factor was the sulfur atom that is present in thiophene and is absent in pyrrole, as it is the analog molecule to thiophene with a nitrogen atom instead. Pyrrole has the ability to plasma polymerize in a same way as thiophene. Therefore, it can be expected that the coated layer of both precursors has a similar structure.

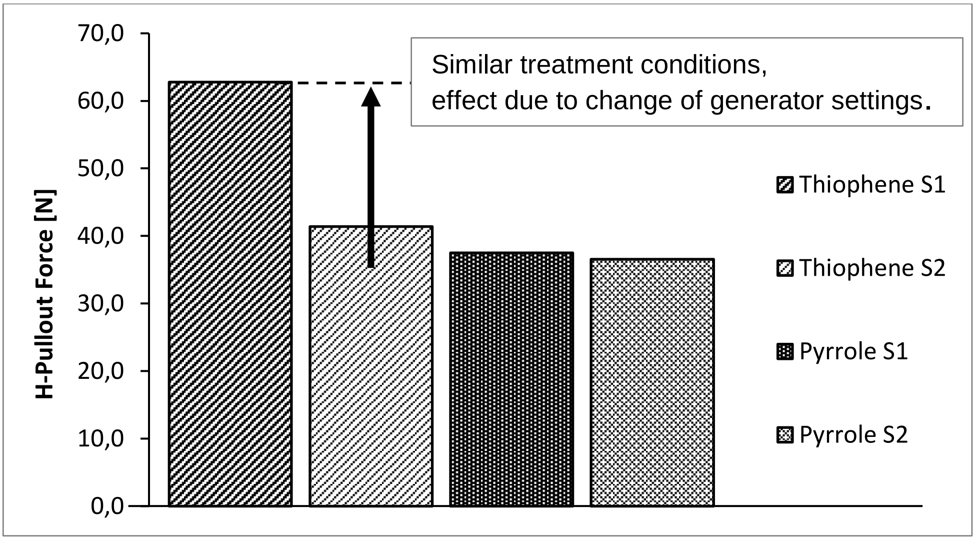


Figure 62: Effect of generator settings on similarly structured precursor molecules.

From Figure 62 it can be seen, that one setting is superior over the others. In fact, the thiophene coating with the maximum plasma power of 4,1 kW (Thiophene S1) generates the best adhesion values with H-pullout values of 62,8 N, which was a new benchmark within this work at that point of time. Apparently, the modification of the suction system enabled the plasma treatment process to gain a significantly better performance over previous trials. The gap of 21,4 N between the S1 and S2 settings is a clear indicator how important proper treatment conditions are. Interestingly, this improvement step is missing in case of pyrrole, where the improvement is within the error range. From this it can be concluded, that also the presence of sulfur in the molecular structure matters for the adhesion promotion. Further, all three mentioned factors (precursor, plasma power and exhaust handling) play a key-role in adhesion generation.

Fully optimized plasma conditions - In Figure 63, a direct comparison of a thiophene plasma coated rayon cord with its untreated equivalent shows how strong the effect of plasma treatment on the adhesion is. Up to an elongation of about 100 % strain, the plasma treated cord can take the load stress, with a peak of ca 70 N. Then the sample fails, and the measured force drops down to 40 N. At a strain of 150 %, another less significant drop down to 30 N happens. Afterwards the cord simply slips out of the rubber. The wave-like pattern is probably an effect of the cord slipping within the rubber matrix. That effect demonstrates that the untreated cord has no interaction with the rubber. The strong adhesion of the thiophene coated cord in conjunction with the peak performance of the cord is a strong indication that the type of adhesion created by the plasma treatment is indeed based on chemical bonding.

The confidence that the adhesion is of chemical nature can be further strengthened with microscopic images of the tested H-pullout samples. The part of the sample where the cord was pulled out was cut in half and analyzed under an optical microscope, a Leica MZ 125. In the image below: Figure 64, a H-pullout sample after testing with a thiophene plasma coating is shown. A considerable number of filaments of the rayon cord are remaining on the rubber surface. This is a strong indication that the area of failure is in the very top layer of the cord surface. Apparently, the outer filaments of the cord break and the specimen fails at the H-pullout test. Fragments of the broken filaments which are bonded to the rubber, remain at the rubber surface and are visible under the microscope. This type of failure is in contrast with the other samples, where no filaments remain on the rubber surface and the samples fail at much lower forces during the adhesion test. It is worth to mention, that the RFL sample used for comparison fails partly in the RFL/rubber interface or entirely in the rubber phase. The latter one, cohesive failure, is clearly the preferred type of failure.

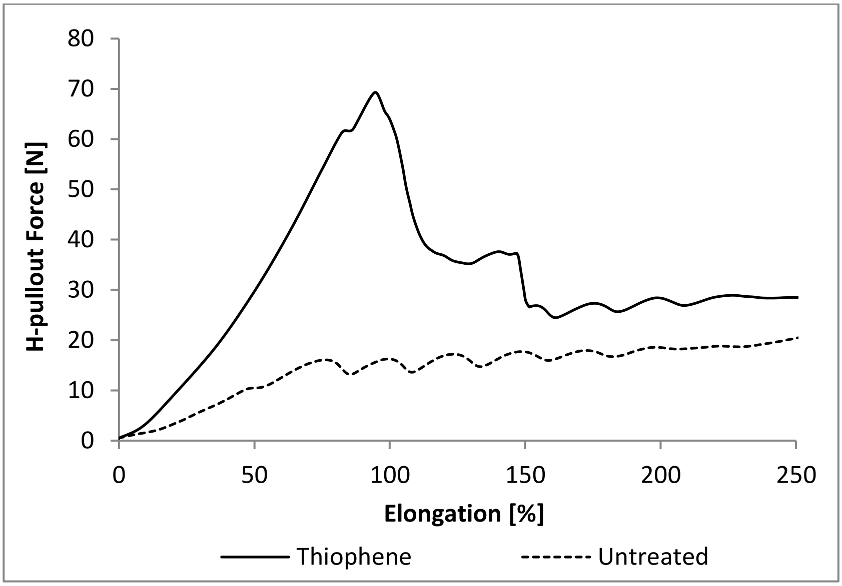


Figure 63: Force-elongation diagram of a plasma coated and an untreated cord in vulcanized rubber.

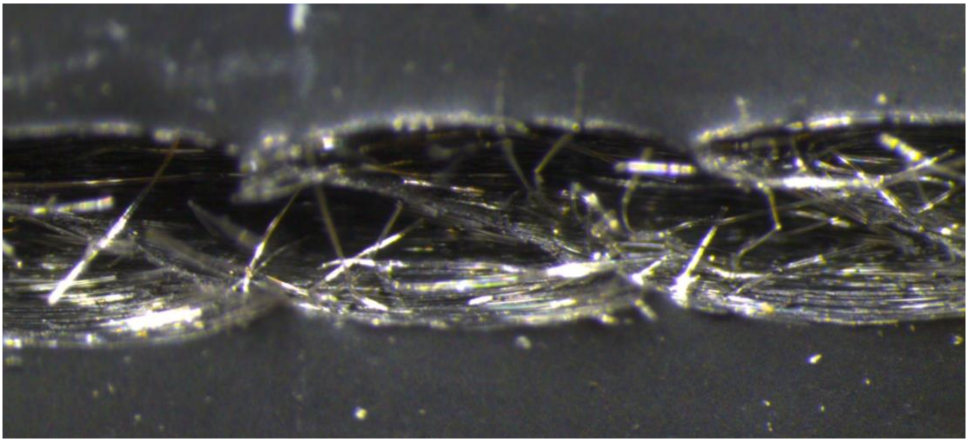


Figure 64: Remaining filaments in an H-Pullout rubber block after testing.

To better understand the importance of each plasma treatment step, several tests were performed, where a specific combination of treatment steps was compared to each other. The results are shown in Figure 65. Apart from the different combinations of plasma treatment, the test conditions remained unchanged.

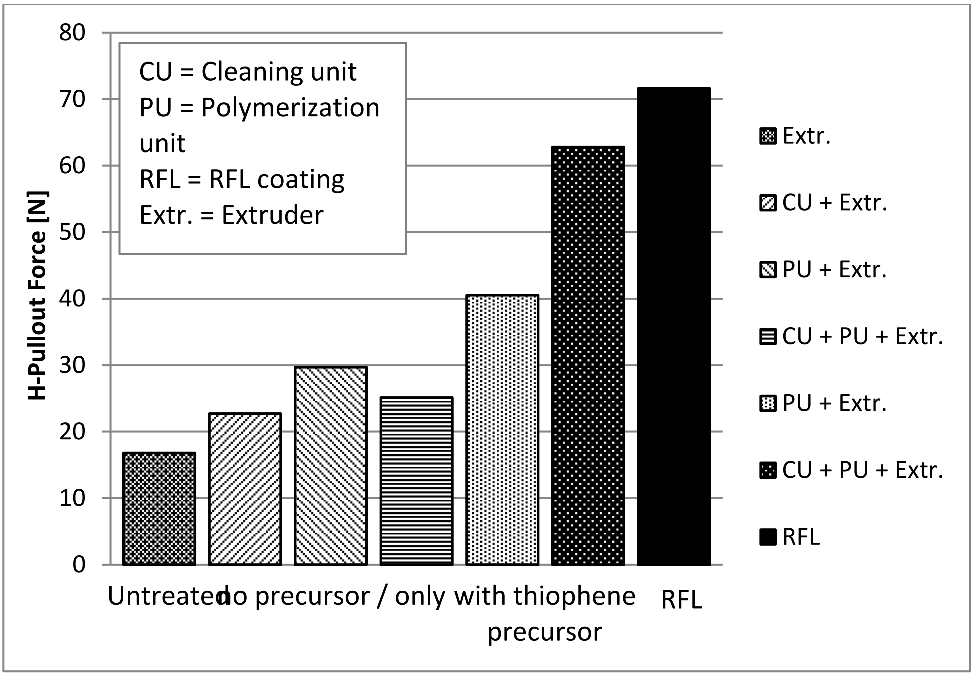


Figure 65: Effect of different treatment steps on the adhesion.

On the left side, the untreated reference is shown, which has clearly the lowest adhesion value. Therefore, all plasma treatment steps do contribute to the adhesion process. That being said, the effect of decontamination is limited to an adhesion increase by a factor of less than 2. The use of only two plasma jets, either the first pair (cleaning unit – CU) or the second one (polymerization unit – PU), has the lowest effect, while the combination of all four plasma jets has a slightly stronger effect. However, if no decontamination is applied, but the PU deposits a thiophene plasma coating, the adhesion improves by a factor of more than two. The best adhesion results are gained when the full plasma treatment capacity is used, which proves that the development steps for the plasma line were correct and necessary. Still, it has to be acknowledged that adhesion created by the plasma is not as good as the one that can be reached with a RFL coating.

Effect of immediate rubberizing with extruder - Because all plasma treatment steps could prove their necessity, it was questioned if the immediate rubber coating is a necessity as well. Therefore, a straight forward comparison of one and the same plasma treatment condition was compared, where one sample received an immediate rubber coating while the other sample did not. The results are shown in Figure 66. Interestingly, the unprotected sample exhibits an even lower adhesion value than a not decontaminated one. It can be concluded, that the immediate protection after the plasma treatment is even more important than a decontamination prior the actual plasma treatment. Overall, it is of high importance to maintain great control over the treatment conditons at any time.

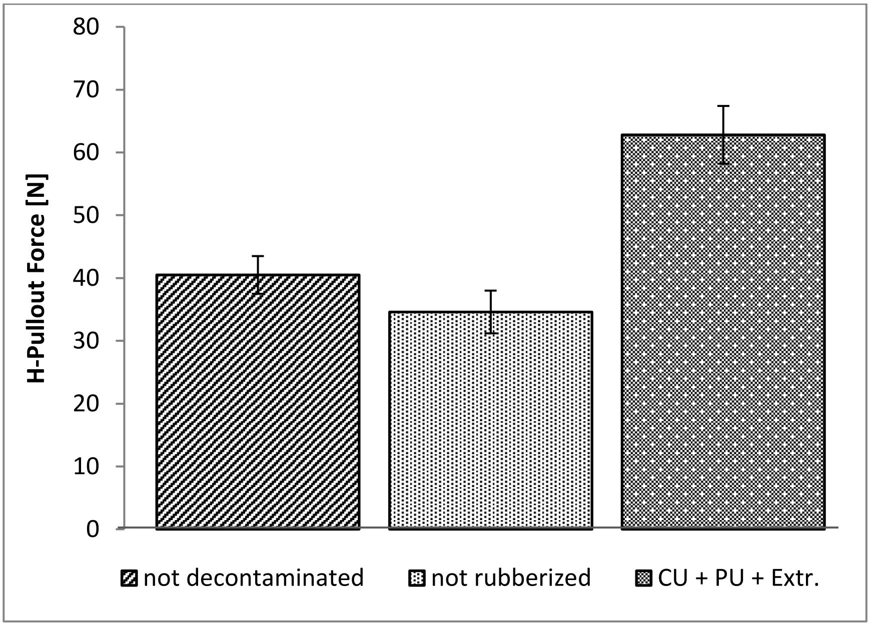


Figure 66: Effect of immediate rubber coating of the cord.

Effect of precursor flow-rate - With a better controlled process, the flow-rate of the precursor was considered again under constant plasma conditions. While the previous test showed only insignificant differences between the flow-rates and plasma power settings, the improved setup shows a clear further improvement. A flow-rate of 50 g/h has a much lower adhesion force of about 43 N than the higher flow-rates. The difference between 100 and 150 g/h is less significant, but is clearly measurable with 15 specimens for each sample. The specimens with a flow-rate of 150 g/h have an average H-pullout value of 63 N and, therefore, have a performance advantage of 4 N over the samples with 100 g/h.

SPAF tests - For practical reasons, the adhesion performance was most frequently performed with H-pullout test. To not entirely rely on that test and to verify those results, SPAF tests were performed at Apollo Vredestein B.V. This test is evaluated in two ways: On the one hand a force-strain diagram is analyzed, where at a strain of 30 % and 100 % the forces are taken as comparison values. On the other hand, the sample is optically assessed, and a rating is given based on how much cord is covered by rubber. This basically means, that the amount of visible interface failure is used to appreciate the rating of the sample. The more cord is visible, the lower the rating will be.

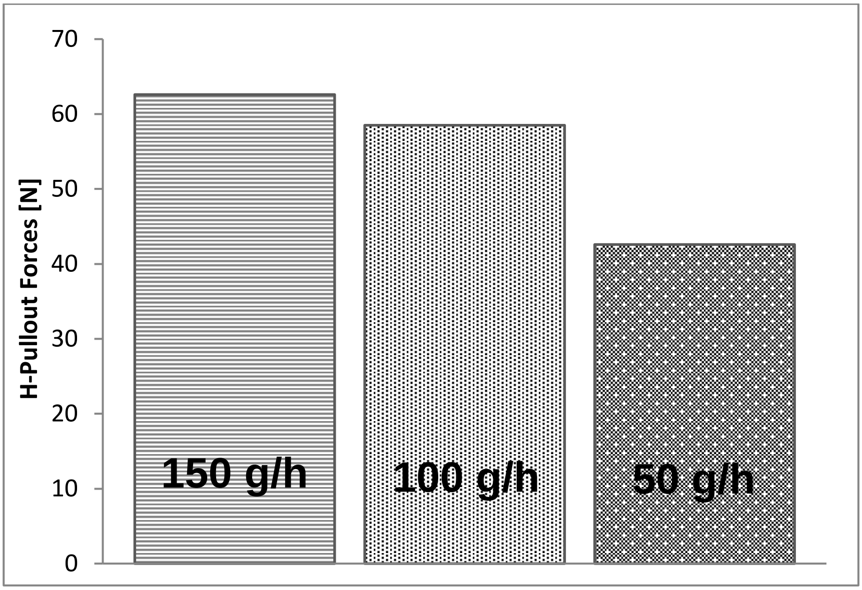


Figure 67: Effect of precursor flow-rate for rayon cord.

In Figure 68, a force versus strain curve obtained with the SPAF test is shown. There are 4 different samples compared. An RFL coated sample is taken as reference, both plasma samples have a thiophene coating, but one received a rubber coating directly after the plasma coating step, the other one not. Finally, an untreated cord is taken as additional reference. The RFL coating exhibits the highest forces and the most distinctive jitter effect. The jitter is generated due to the high stress that is occurring in the composite during the test. The higher the stress, the more distinctive the jitter will be. In case of the RFL sample the failure is almost entirely on the rubber side. Only a few spots are detectable which indicate a failure in the cord-rubber-interface: see Figure 69.

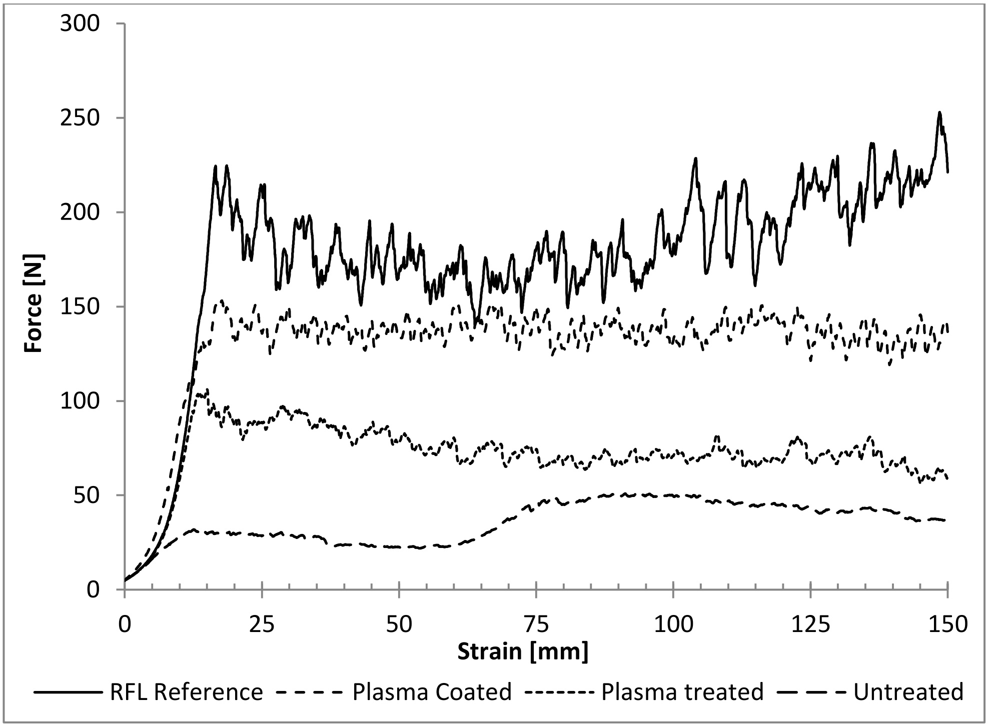


Figure 68: Results of the SPAF test of differently treated cord samples.

All the RFL samples have a certain “banana” shaped curvature: see Figure 68, with a minimum in force value at about 60 % strain. This behavior was not detectable in case of the plasma treated and rubberized sample. These samples have a steady force level that doesn’t change during the test. The jitter is less distinctive compared to the RFL sample. The overall performance is closer to the RFL reference than it appeared with the H-pullout test. Nevertheless, the trend shown from both tests is identical. The optical judgement of the plasma treated and rubberized specimens unfold a different picture than the force-strain diagram. A significant amount of cord is visible at the failure interface, clearly indicating that the samples tend to fail at the cord-rubber interface; they show adhesive breakage. Even though the measured performance is reasonably good, the type of failure is not the desired one. The reason for this failure mode will be further analyzed and discussed in Chapter 6. The non-rubberized plasma sample performs clearly inferior. This is true for both categories, the mechanical measurement and the optical judgement. The adhesion between cord and rubber is less and, therefore, the primary failure mode is adhesive, failure at the cord-rubber interface. This is also visible for the jitter, which is much less concise.

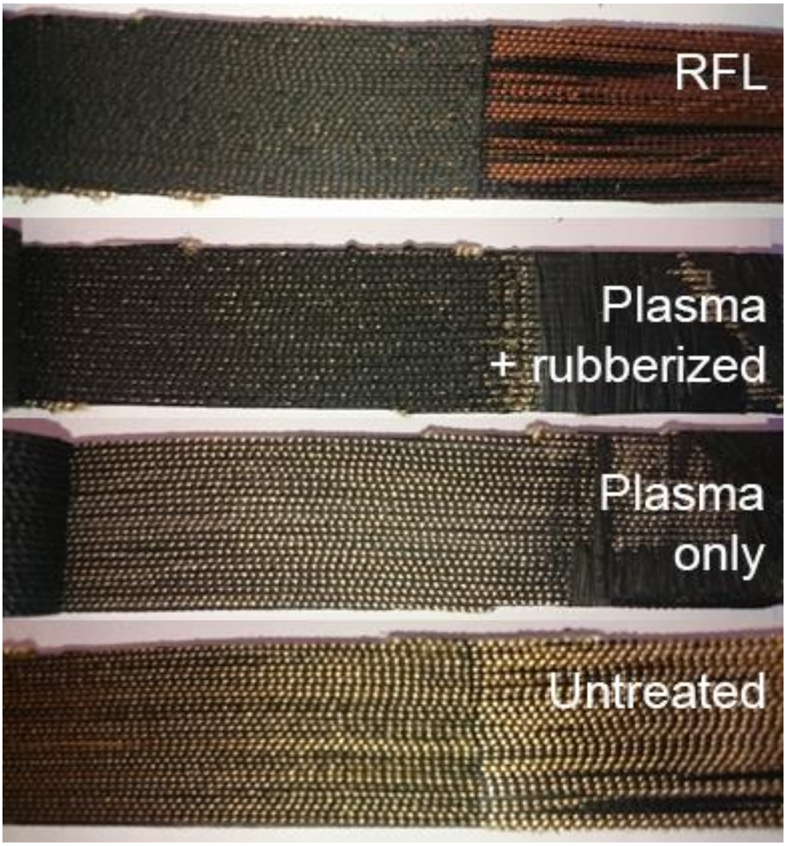


Figure 69: Samples of the SPAF test after testing to evaluate the failure interface.

The forces generated by the test cannot be transferred to the cord and that prevents higher stresses in the composite. The untreated cord is entirely unable to transfer forces and has no jitter at all. There is no reinforcing effect measurable and as a matter of fact, no adhesion between cord and rubber detectable. This can also be seen in Figure 69 (untreated), which unveils a complete interface failure. The rubber was pressed tightly to the rubber surface during vulcanization, as the cord surface is accurately imaged on the rubber surface, but even this intimate contact is not able to build-up a good rubber-cord interaction which is able to transfer any forces. From 75% strain onwards, the force level increases noticeably. The reason for that remained unclear.

4.3.2 Polyester

Parallel to the work that was done on Rayon, also Polyester cord has been used in the present project. The Polyester cord had 1100 dtex in a x2 configuration and was supplied by Svenskt Konstsilke, Boras, Sweden. Clearly, this type of cord has very different material properties than Rayon, for example its glass transition temperature, shrinkage behavior, surface characteristics (inertness) and functional groups, to just name a few. Because of that, it was expected that polyester would require different treatment conditions, with respect to the settings of the plasma line. The backbone structure of Polyester (Polyethylene Terephthalate (PET)) is shown in Figure 70. Unlike Rayon it has no hydroxyl functional group and the oxygen groups contribute to its inertness.

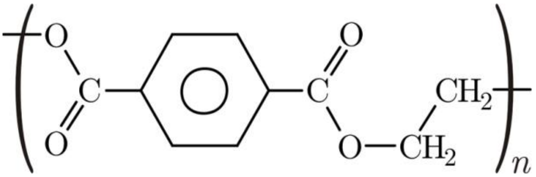


Figure 70: Repeating unit of polyethelene terephthalate.

Indeed, an initial test showed, that the polyester reacted far more sensitive to the plasma treatment than Rayon. If the cord was pulled with a to low speed through the plasma flame, immediately severe surface defects occurred: the outer filaments were cut and melted to form small particles. Furthermore, the stiffness of the cord significantly increased by the plasma treatment, which made it almost brittle. That effect of the treatment made it difficult to find suitable settings, as a relatively high pull speed effectively reduces the efficiency of plasma coating. A reduction of the plasma power instead of an increased treatment speed did not help either, because the influence on the actual treatment temperature is too small.

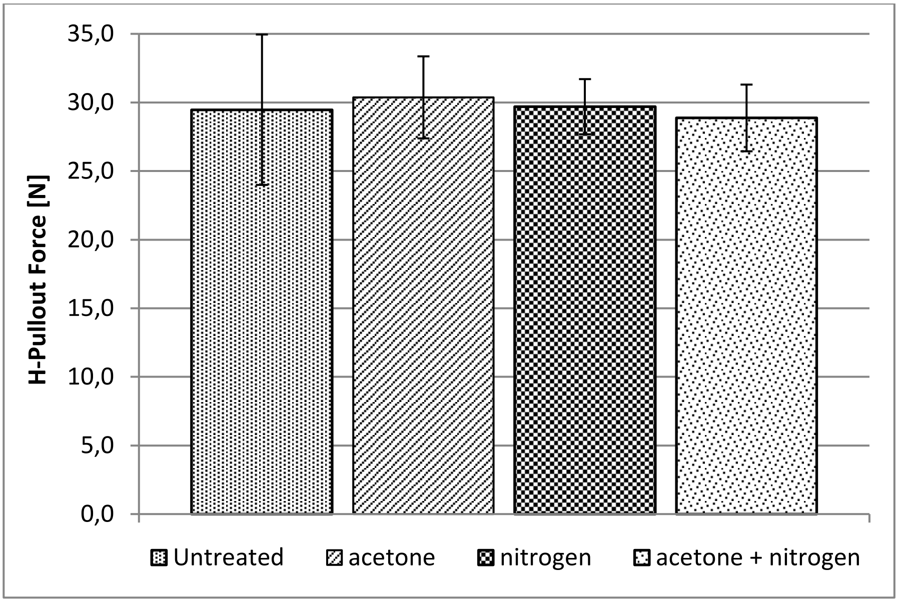


Figure 71: Adhesion values of PET cord with different treatments

Attempts to clean the PET cord with acetone and nitrogen plasma to remove residual processing aids did not show any increase in adhesion forces: Figure 71, while a certain decrease of the variance of those values was noticeable. The necessity to clean the cord before the actual plasma treatment is, unlike with Rayon, apparently not essential. Still, potential residues from the cord production process will not contribute to a better adhesion. Therefore, the same APPJ configuration like with Rayon has been used. The small decrease in variance of the adhesion values was taken as indirect indication, that doing so will contribute to the success of the treatment.

Table 12: Plasma treatment conditions for polyester.

Precursor	m/min	Flow rate	Evap. temp.	Plasma settings*	Condi-tion	Gas
Thiophene	15	150 g/h	90 °C	100/25/100	dry	N2
Diallyl-disulfide	15	150 g/h	195 °C	100/25/100	dry	N2
Dimethyl-trisulfide	15	150 g/h	180 °C	100/25/100	dry	N2

***Plasma generator settings in Voltage [%] / Freq. [kHz] / Cycle time [%]**

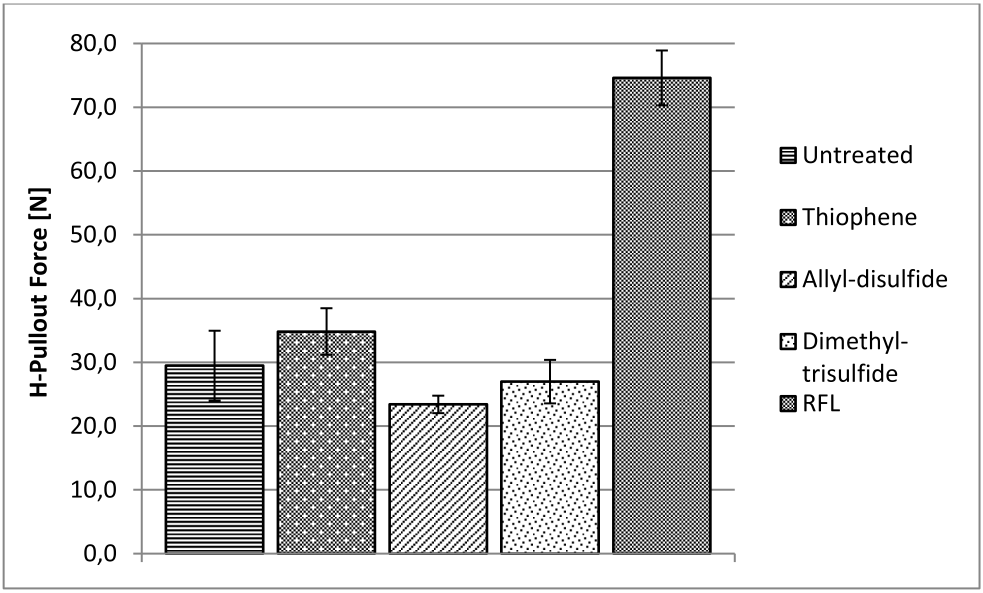


Figure 72: H-pullout test results for PET cords with sulfur-based precursors.

The effect of Polythiophene on polyester cord is shown in Figure 72. A comparable treatment result like with Rayon cord is not observed. Only a minor positive effect is noticeable with thiophene as precursor, which is just slightly above the error of the measurement. The other sulfidic precursors even decrease the H-pullout force values. The cause of this phenomena is a combination of the materials' inertness with the treatment conditions, which did not allow a more aggressive plasma setting. The consequence is, that under these circumstances it is not possible to improve the adhesion of polyester cord to rubber.

4.4 DISCUSSION AND CONCLUSIONS

In this chapter, several sulfuric precursors were evaluated. The aim was to plasma polymerize these precursors to form a surface layer on the cords, and also to react with the cord surface to form a strong bonding due to active radicals on the surface. This layer should adhere due to its covalent bondage to the cord and enhance adhesion towards rubber, because the plasma polymerized layer itself would reduce the polar nature of the cord, and its sulfuric groups could interact with the rubber during vulcanization. Several mono- and polysulfidic precursors were tested.

A strong increase of adhesion between rayon and rubber was achieved with thiophene as precursor. The enhancement was measured by two mechanical testing methods: the H-pullout test and SPAF test. While the improvement was significant, it nearly reached the desired level of a RFL-coated cord. The failure mode was clearly different. While in case of RFL treatment, the failure occurred cohesive, thus mainly in the rubber phase, this was not the case for the PT methods. In the latter case, the outer filaments of the cords failed first when a load was applied. Yet, the remaining filaments in the rubber phase can be seen as an evidence of chemical adhesion. Therefore, the achieved results with Rayon cord were successful, even though the desired adhesion level was nearly reached with the given plasma line.

Several attempts were made to analyze the polymerized layer in detail. In literature, mainly FT-IR and XPS techniques are used for that purpose. This analysis would help to understand, why certain precursors weren’t able to promote adhesion. However, those techniques were unable to indicate differences between untreated cord and its plasma treated counterpart, while mechanically the effect of the plasma treatment was clearly measurable.

The requirements for the plasma precursor for adhesion promotion with Rayon cord were well defined in this work. Experiments with different sulfuric precursors clearly showed, that thiophene alone could significantly improve cord-rubber adhesion. Its unique characteristic property over the other precursors is the ring-structure in its molecular configuration. The structure of thiophene gives the best reactivity when exposed to the plasma. It is proposed that other sulfuric precursors get entirely atomized in the plasma and recombine in a chaotic manner. The created plasma polymerized layer on the cord surface has no repeating elements and probably only a limited number of functional groups, that can react with the rubber during vulcanization. Therefore, their ability to adhere to an elastomeric matrix is limited. Thiophene can plasma polymerize with a more stable molecule that is easier to activate. Consequently, the created polymeric layer has many more repeating units with a significantly higher number of functional groups, resulting in the ability to create a significantly higher level of adhesion. A comparison of thiophene with pyrrole, which has a similar molecule structure, in which the sulfur atom of the thiophene is substituted by a secondary amine in case of pyrrole, indicated the importance of a sulfur atom in the ring. While thiophene performed well, pyrrole could enhance the adhesion level only slightly. Clearly, the sulfur atom of thiophene helps with the interaction of the plasma polymerized layer with the formed sulfur complexes during vulcanization. Another comparison of thiophene with tetrahydrothiophene further underlined the importance of double bonds in the ring structure, which are entirely absent in case of tetrahydrothiophene. As the name indicates, the additional presence of four hydrogen atoms prevents the reaction of the double bonds. This causes a less stable ring which probably gets cracked during the exposure to the plasma and prevents a similar plasma polymerization like thiophene.

Besides those requirements for the precursor molecule, it was found that a plasma treatment with nitrogen prior to the precursor is necessary to achieve good adhesion results. It was not only important to use nitrogen as ionization and precursor gas, but also to create a protective atmosphere around the cord until it came in touch with rubber. The much higher reactivity of oxygen when using air as ionization gas deactivated the freshly plasma treated cord and therefore, prevented a successful bonding of the plasma polymerized layer with the rubber. Further, the plasma power setting of the generator and the precursor flow rate turned out to have a strong influence on the adhesion values.

The treatment of polyester cord with sulfuric precursors did not show any positive effect, even when the optimizations achieved with Rayon where applied. Clearly, polyester is a very heat sensitive material, which prevented aggressive plasma settings, which would have been necessary to overcome the materials inertness. As the sulfuric precursor plasma treatment was not applicable for polyester, another inventive plasma solution was developed for polyester, which is described in the next chapter.

CHAPTER 5

Silane precursors:
A novel approach of promoting adhesion of reinforcing cord to elastomers.

This chapter covers an adhesion concept where the cord surface will be modified by a plasma treatment in such a way, that a silicate structure with hydroxyl and ethoxysilane functional groups is deposited on the cord surface. These moieties are expected to allow coupling agents to attach to the cord and later react during vulcanization with the rubber matrix. This would establish interfacial covalent bonds and create strong adhesion between cord and rubber.

5.1 INTRODUCTION

Silica technology is well known in the tire industry since Michelin introduced the green tire concept in 1992 [98]. This was a breakthrough, as this technology allowed a reduction of rolling resistance and at the same time an improvement in wet grip. Therefore, it allowed to overcome a balance problem: whenever a tire was improved in terms of one of the properties - wet grip, rolling resistance and abrasion resistance or wear – the two other properties were compromised. However, application of silica in passenger car tire treads was a major challenge for the tire industry, as it required a new mixing technology and new handling procedures for silica compounds. Nowadays, it is standard technology for a European passenger car tire tread.

What makes silica technology work in a rubber compound are coupling agents. Without them, silica would be a poor filler material with strong tendency of agglomeration. Coupling agents are chemicals, which can react with the hydroxyl groups on the silica surface. Ideally, they would cover the whole silica surface with a hydrophobic layer, which prevents agglomeration and results in an improved compatibility and incorporation. When the rubber compound is vulcanized, the coupling agents react with the rubber as well, as they have two different types of functional groups linked together: one to couple with the silica surface and another one to react with the unsaturation of the elastomer molecule.

This approach can also be applied to a reinforcing cord. With plasma treatment, the deposition of a silica structure on the cord surface is possible. The challenge is to find a proper procedure to introduce the coupling agent and to let it react with the cord. In a rubber compound containing silica, this silanisation reaction is performed during the mixing process, where the temperature is raised to about 140 °C. This temperature is high enough to let the silanisation reaction take place at a reasonable rate, but is still low enough to avoid degradation of the elastomer. In the final productive mixing step, the vulcanization system is added. Clearly, it is not possible to apply this procedure for the silica coated cord. Therefore, the silanisation must occur either in an additional processing step between plasma treatment and vulcanization, or during the vulcanization.

This chapter describes how the plasma treatment has been done for both, Rayon and PET cords, and which solutions for the incorporation of the coupling agent have been explored. Besides that, an alternative plasma treatment to the silica coating is introduced and a Design of Experiments was applied on the coupling agent incorporation. Overall, the potential of this adhesion promotion technology is unveiled, and future research fields are discovered.

5.2 SILANE PRECURSOR

As precursor tetraethyl orthosilicate (see Figure 73), also known as tetraethoxysilane or TEOS in abbreviated form, was selected. It is a colorless liquid with a sharp and alcohol-like odor. Its chemical formula is $SiC_8H_{20}O_4$ and is the ethyl ester of orthosilicic acid. It has a molecular weight of 208,33 g/mol and a density of 0,933 g/ml at 20 °C. The melting point is -77 °C and the boiling point is reached at 196 °C [99]. In the industry, it is widely used as silica source, as base-product for coatings and in aerogels.

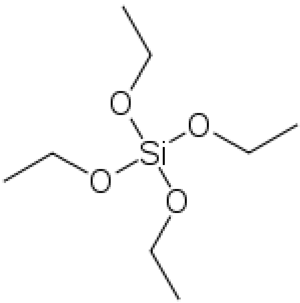


Figure 73: Tetraethoxysilane (TEOS)

TEOS is the reaction product of silicon tetrachloride and ethanol and has a tetrahedral molecular structure due to the centered silicon atom. It is insoluble in water, but very well soluble in ethanol. Adding water to TEOS, it undergoes a hydrolysis reaction. Under neutral conditions, this is a very slow reaction, which can be accelerated by either acidic or alkaline conditions:

$$C_8H_2O_4Si \quad + \quad 4\ H_2O \quad \rightarrow \quad H_4SiO_4 \quad + \quad 4\ C_2H_5OH \qquad (1)$$

The reaction shown in (1) is a hydration process, which liberates ethyl alcohol. The intermediate product can be further condensed to form an oligomeric pre-polymer, which is often used in coatings, or converted further to silicon oxide SiO_2. Using the Stöber process, the creation of monodisperse SiO_2 is possible with a good control over the particle size. The control parameters are concentration, temperature and ammonia content, and the particle size is in a range of 20 to 500 nm.

TEOS can be applied in a plasma process in two ways: It is either used in its pure form or, as described above, in a mixture with ethanol and a certain amount of distilled water. The former option takes a scission of the molecule in the plasma into account. A recombination of the TEOS fragments on the cord surface could create siliconoxidelike structures while still featuring ethoxysilanes. In the latter option, next to interaction with the plasma, a hydrolysis reaction can also be expected when exposing the mixture to plasma. Both, the creation of an oligomeric pre-polymer as well as monodisperse silicon oxide particles can potentially occur.

5.3 EXPERIMENTAL

From an experimental point of view, the silane precursor approach involves more steps than the plasma treatment with sulfuric precursors. These steps are as follows:

a. Plasma treatment with silane precursor,
b. Dipping process with coupling agent,
c. Controlled drying of the dipped cord,
d. Co-vulcanization of dipped cord and rubber.

There is a time-delay between step a and b due to the fact, that the plasma treatment was performed at VMI in Epe, while the dipping process was done in the chemical lab of the University of Twente. Unlike for sulfuric precursors, the contact of the freshly plasma coated cord surface with the environment is not harmful in the case of a silane precursor. Therefore, a simple wind-up and transportation in plastic bags of the cord was possible without compromising the adhesion performance.

The plasma treatment of the cord was performed as described in the previous chapter with a decontamination step directly followed by the actual plasma coating step. However, the latter step was in this case done with an air plasma. More precisely with filtered compressor air as ionization gas. The precursor supplier gas must always be nitrogen, and for the decontamination plasma nitrogen gas was used as well. A voltage of 278 V and a current of 5,8 A were applied for the initial cleaning treatment step.

The plasma coating settings were as follows: the precursor flow rate was set to 150 g/h and the evaporation temperature to 200 ˚C for all experiments in this chapter. For the plasma generator itself, two settings were used: strong plasma settings called S1 and weaker plasma settings called S2. The actual values of these plasma settings can be seen in Table 13.

Table 13: Plasma coating settings for TEOS.

Plasma	Voltage [%]	Frequency [kHz]	Cycle time [%]	Actual voltage [V]	Actual current [A]	Calculated Power [kW]
S1	100	25	100	296	12	3,5
S2	85	20	66	259	9	2,4

The cord speed, thus the treatment time, was widely ranged in the case of Rayon with 30, 15, 7,5 and 3,75 m/min. For PET, a minimum speed of 10 m/min had to be chosen to prevent thermal damage of this temperature sensitive cord. Therefore, the cord speed for PET was 30, 20 and 10 m/min.

Besides the plasma treatment, the application of the silane coupling agent is an important factor, too. A commonly used coupling agent in the tyre industry is TESPT with the chemical name bis-[3-(triethoxysilyl)propyl] tetrasulfide, which is shown in Figure 74. The triethoxysilyl groups, which are located on both ends of the molecule, may react with the silanol groups of the silica on the cord surface. This reaction forms siloxane bonds in a primary reaction step under creation of ethanol as side product [100, 101]. The polysulfane chain segment in the middle of the molecule with an average sulfur chain length of 3,8 (actually a mixture of sulfanes from S_2 to S_{10}) is not temperature-stable. It breaks apart under elevated temperatures during vulcanization. That liberates free sulfur and creates two highly active bonding sites for the cross-linking sulfur complexes formed during the vulcanization reaction. These react with the TESPT fragments and with the rubber chains. This reaction mechanism creates a bonding of the plasma coating via siloxane bonds with the TESPT, which is further bonded via sulfur bonds to the rubber matrix. Therefore, the system provides a chemical bonding between cord and rubber.

As an alternative to TESPT, a second coupling agent called MPTES (mercapto-propyl-triethoxysilane) was used as well for comparison. It features only one triethoxysilyl group and instead of the sulfur chain segment, it has a highly reactive mercapto group (S-H), that terminates the molecule on the other side (see Figure 75).

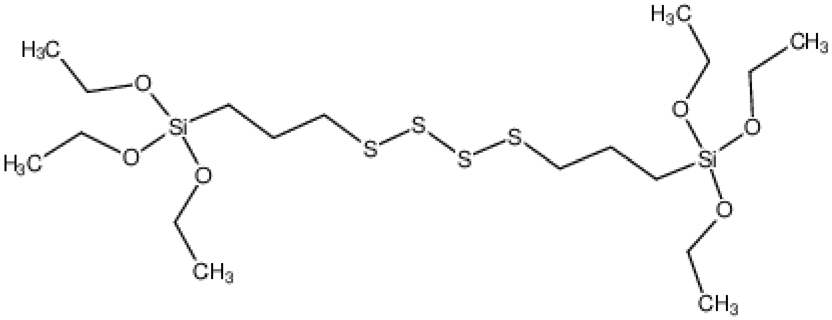


Figure 74: Silane coupling agent TESPT (bis-[3-(triethoxysilyl)propyl]tetrasulfide)

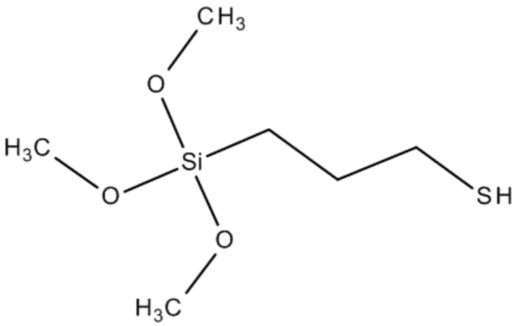


Figure 75: Silane coupling agent MPTES (mercapto-propyl-triethoxysilane)

Two different methods were studied to incorporate the coupling agents:

I. Incorporation of the coupling agent directly into the rubber as an ingredient of the compound. This was done on a two-roll-mill using the reference compound. As the required amount of coupling agent for a successful cord-to-rubber bondage was unknown, two concentration levels were used: 2 and 5 weight percentage (w%) of TESPT, where 5 w% is equal to 9.2 phr. A disadvantage of this method is, that the silanisation process must occur in the rubber phase during vulcanization. This is certainly an undesired situation: It is a problem, because the ethanol as side product cannot evaporate easily under these circumstances and will probably partly stay in the rubber. This will cause porosity later on in the test specimens and may even affect the adhesion values. Ideally, the

TESPT modified compound would only be used for the rubber coating of the cord, which certainly would be the case in an industrial production scenario. Unfortunately, the circumstances for drying and rubberizing the dipped cord in this study did not permit this approach.

II. A dipping bath containing the coupling agent was used to deposit the latter on the TEOS coated cord. Consequently, after the dipping step a drying step in an oven is required. While drying the cord, the silanisation reaction can take place and the ethanol as reaction side product can easily evaporate. The previously mentioned disadvantage of having ethanol residues trapped in the rubber is therefore avoided. Afterwards, the so prepared cord was vulcanized together with the unmodified reference rubber compound. The initial dipping was done with the Bath I composition, which was prepared according to the recipe shown in Table 14. As buffer, either acetic acid or triethylamine were used, as the entire process would run very slow under pH-neutral conditions. However, only lesser amounts of catalyst are necessary to accelerate the reaction. The same applies to the coupling agent, where rather lesser amounts improve the deposition process towards the cord, while too high concentrations could cause the TESPT to oligomerize instead of a reaction with the OHgroups on the cord surface. The dipping was performed in the lab using standard equipment. Dipping time was 60 minutes under room temperature conditions in a closed embodiment.

Table 14: Dipping recipes used for both cords (TESPT and MPTES used for Bath I; TESPT for Bath II)

Ingredients	Bath I	w%	Bath II	w%
Ethanol	50,0 g	92,9	22,2 g	80,0
Demin. water	2,6 g	4,9	4,0 g	14,4
Coupling agent	1,1 g	2,0	1,0 g	3,6
Catalyst	0,1 g	0,2	0,6 g	2,0
	53,8 g	100,0	27,8 g	100

Drying process: To finalize the TEOS coating and coupling agent dipping step, it is necessary to activate their chemical reaction via heat. The cords were taken from the dip and allowed to dry at room temperature for 10 minutes. After that, the cords were mounted on a custom-build frame that features a clamping system, which maintains a certain tension of the cord. This is beneficial, as the cords get stiffer due to the treatment. Besides, the cords tend to stick together during the drying process when they are in touch. All cords were dried in the oven at 100 ˚C for 15 minutes.

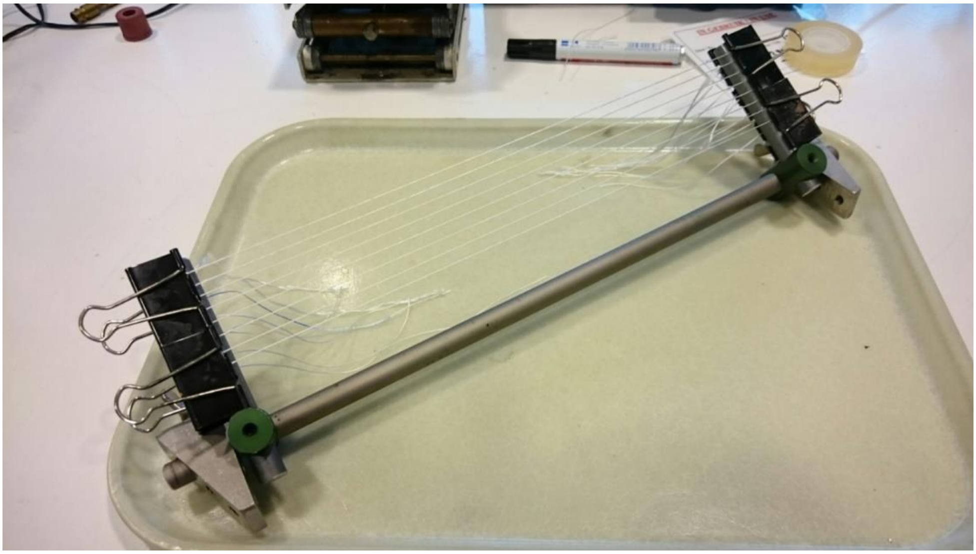


Figure 76: Custom-made frame to dry the cord while providing a slight tension to define a straight shape once the dipping was applied and dried.

5.4 RESULTS AND DISCUSSION

5.4.1 Rayon cord

The plasma settings S1 and S2: see Table 13, were used with a steady TEOS supply of 150 g/h in combination with various treatment speeds. With the application of the incorporated TESPT method, it was planned to select an optimal treatment speed for a series of experiments. However, it was found in the pre-trials, that the two different plasma settings and the treatment speeds had no significant influence on the adhesion results, which were measured with H-pullout tests according to ASTM D4776 (see Chapter 4). While the adhesion slightly improved by the TEOS treatment with either plasma treatment, it clearly was lower than the one of the RFL treated cords. One could expect significant differences when changing test variables like the plasma strength or the treatment time. That the effect remained insignificant might be explained by the settings, as both settings, S1 and S2, might atomize the TEOS molecule and therefore, no difference is seen between the two settings. The same might be true for the treatment time: the missing effect could be explained with a sufficient coating which is already reached at higher cord speeds, thus shorter treatment times.

The experiments illustrated in Figure 77 were done under these consistent plasma treatment settings:

Plasma power setting:	S1
Treatment speed:	10 m/min
TEOS flow rate:	150 g/h
Evaporation temperature:	200 °C
Pre-drying of cord:	no

For a better understanding of the results, the samples shown in Figure 77 are marked with the following scheme:

- The ascending dashed bars represent the bath I dip process (each type a different catalyst);
- Horizontal dashed bars stand for the incorporated method, with a coupling agent amount of 2 w% and 5 w%, respectively, added to the compound;
- The declining dashed bars show the values for the bath II dipping process (each type a different catalyst).

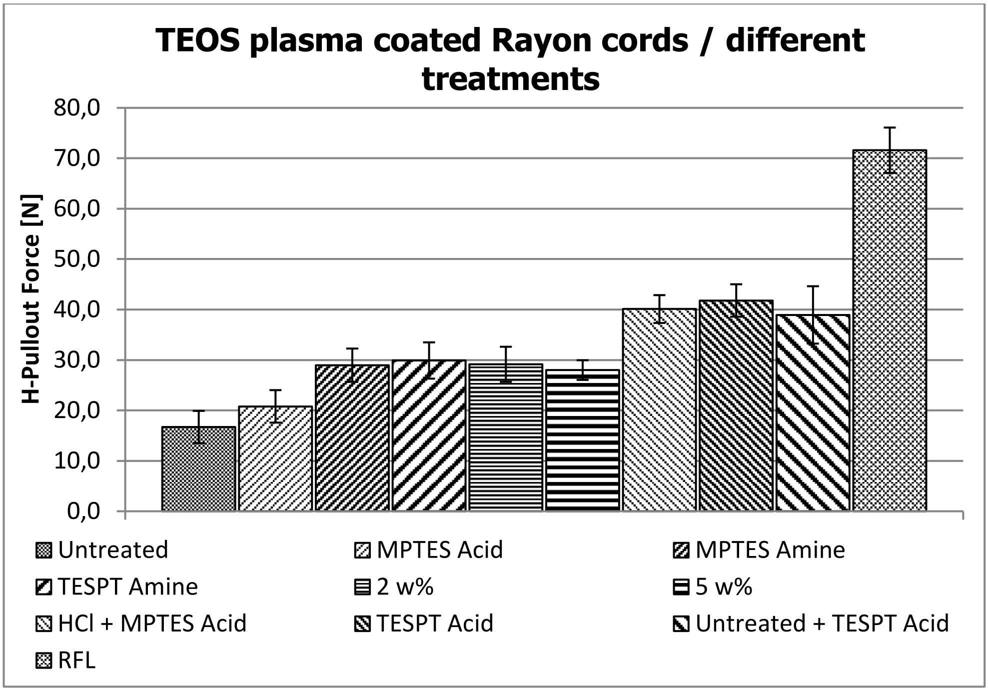


Figure 77: H-Pullout results for TEOS-plasma-coated Rayon cords.

Clearly, the untreated rayon cord did show the lowest adhesion (16,7 N). Dipping the cord in a MPTES/acid mixture (type bath I) had nearly no effect as the adhesion reached 20,8 N, while using the MPTES/amine mixture gave slightly better results (29 N). Almost the same result with 29,9 N was achieved with a TESPT/amine dip (type bath I). In comparison with the sulfur precursor or even the RFL version, the results were comparatively low. Two causes are possible: either the coating with TEOS itself was unable to deposit properly on the cord, or the deposited layer did not have a enough OH groups to allow a strong interaction with the coupling agents.

The method with the incorporated TESPT confirmed the adhesion level of the bath I type test specimens. With 2 wt% TESPT incorporated into the compound, the H-pullout force is 29 N and with 5 wt% it is 28 N. That indicates, that 2 wt% of TESPT in the rubber compound were sufficient to make full use of the hydroxyl groups present on the cord surface after the plasma treatment. To see if the plasma deposition itself is inadequate, or if interaction with the coating is missing due to a lack of hydroxyl groups, the following measures were made:

a. Repetition of the bath I type dipping with a small amount of hydrochloric acid (HCl) added. HCl donates H^+ ions, which can react with oxygen to increase the number of available OH groups;
b. Dipping the cord in bath II with an increased amount of demineralized water and acetic acid, which is expected to increase the number of available OH groups.

Compared to the previous results, the adhesion increases roughly by 10 N with the adjusted methods (declining bars). This supports the assumption that more OH groups are necessary to improve the number of formed siloxane bonds.

However, using an untreated cord in the as-delivered state just dipped in a type II bath, see Figure 77: Untreated + TESPT/Acid, nearly gives the same results as a plasma coating, see the same Figure: TESPT/Acid. However, the standard deviation is higher for the untreated cord. This indicates, that the plasma may harmonize the cord surface to a certain degree allowing more steady results in mechanical tests. But more important, it clearly shows that the plasma deposition of TEOS was not successful on Rayon cords. The fact that the untreated cord is relatively responsive to the coupling agent can be explained by the surface chemistry of Rayon cords which contain already a high number of hydroxide groups. However, compared to the RFL coating, the H-pullout forces are in general still far lower. The aim for future work in this field must clearly be to increase the number of available reactive OH groups, either by a suitable plasma treatment of the Rayon cord resulting in a hydroxide rich coating, or by creating conditions that enable TEOS coatings with more OH groups. There are several possibilities that can be explored, like moisturizing the cord, inject water vapor into the plasma reaction chamber or using a mixture of nitrogen and hydrogen as ionization gas.

5.4.2 Polyester cord

The backbone chain of polyester does not have hydroxide groups in its structure: see Figure 78, and the cord itself does not take up moisture from the environment. These properties differ from the ones seen with Rayon cord and decrease the possibility of forming OH groups on the cord surface when applying a TEOS plasma coating. Knowing the results of Rayon introduced in the previous section, it seems difficult to achieve better results with a PET cord.

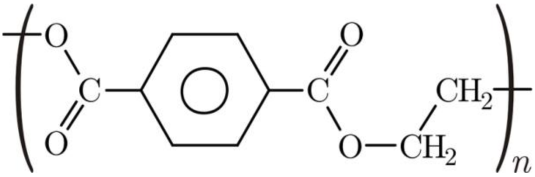


Figure 78: Structure of the polyester backbone.

Like for Rayon, also the PET results with different treatment times and plasma strengths did not have a significant effect on the adhesion results. For a better comparability, identical settings to Rayon have been used for the further TEOS trials. The results of the experiments are illustrated in Figure 79 and were done under the same consistent plasma treatment settings as previously with Rayon cord:

Plasma power setting:	S1
Cord speed:	10 m/min
TEOS flow rate:	150 g/h
Evaporation temperature:	200 °C
Pre-drying of cord:	no

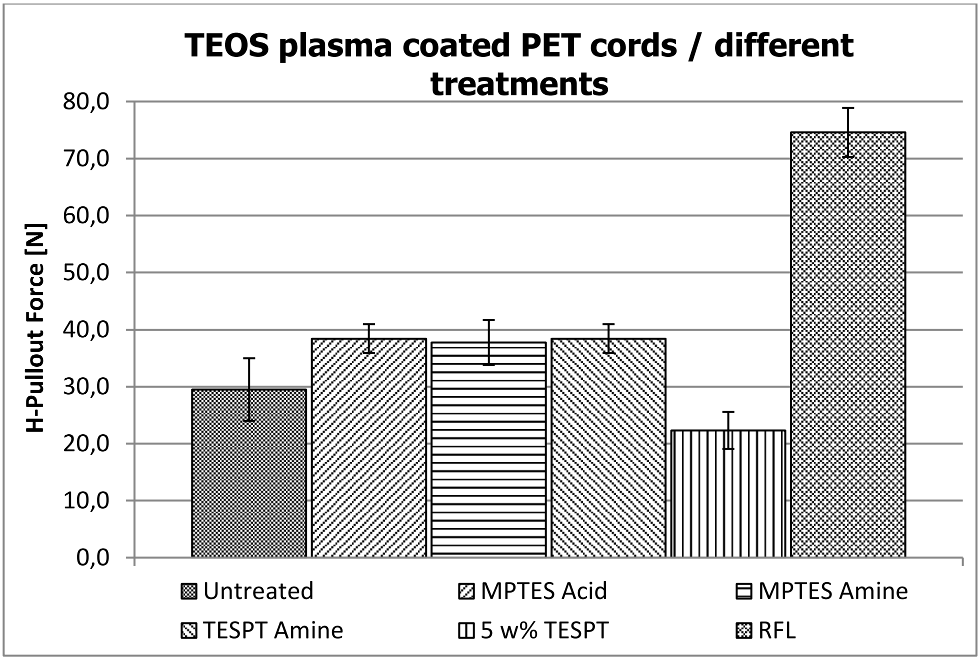


Figure 79: H-Pullout results for TEOS-plasma-coated polyester cords.

For a better understanding of the results, the samples are marked with the following scheme:

- The ascending, horizontal and declining dashed bars represent the type I bath dipping processed cords with different catalysts and coupling agents.
- And the vertical dashed bar stands for the incorporation method, where the coupling agent is mixed into the rubber phase with an amount of 5 wt%.

Clearly, the TEOS coating itself does not provide enough OH groups. This can be seen from the horizontally dashed bar, that represents the test specimens with 5 w% TESPT coupling agent incorporated into the compound. The adhesion value is even lower than the one of the untreated sample. The plasma treatment did not increase the number of hydroxide groups, therefore, the TESPT present in the rubber compound was not able to react in the planned manner. Consequently, the interaction with the cord surface was low. This is in contrast with the Rayon results, as that material showed better values with this treatment.

The PET results achieved with the type I bath dipping process are better. Here the PET cord reaches even higher H-pullout forces than the comparable Rayon cord. However, also the untreated PET cord shows a better adhesion than the corresponding Rayon test specimen. In that perspective, the gained results are equally deficient. The differences between the cords are still interesting, as one would expect less interaction of the inert PET cord, but the opposite is the case.

To achieve further improvements with this type of treatment it is necessary to convert more functional groups of the silica coating from a siloxane type to a silanol type, so that the coupling agent can react with them. Another approach could be to not use a silica coating, but to introduce more hydroxyl groups in a different way; for example, by using demineralized water as precursor. The expected effect is that additional OH groups would be directed outside the cord surface and thus available for silanisation with coupling agents, while the original OH groups are directed into the fiber structure and therefore sterically hindered.

5.4.3 Applying H_2O as precursor instead of TEOS

Before the TEOS trials were performed, it seemed very suitable to use such a precursor as an anchor point for the coupling agent. However, the trials unveiled, that this method lacked in generating enough hydroxide groups for the coupling agent to react with. As an alternative, a direct approach with demineralized water might be a better and easier way to create hydroxyl moieties.

The advantages of water over TEOS are significant: Besides the highly-desired fact, that it delivers a huge number of hydroxide groups, it does not show the drawbacks of many other chemicals used as a plasma precursor such as health risks, smell and high costs. The evaporation temperature of the relatively small water molecule is with 100 °C much lower than of most other precursors. This makes it from a technical point of view much easier to evaporate sufficient amounts of precursor before it enters the plasma jet. The supply is very easy, and there are no concerns towards handling of precursors by an operator. There are no health concerns or REACH restrictions and no environmental burden, besides the fact that water is becoming a more and more valuable and tight resource.

When it comes to the actual plasma treatment process, the plasma treatment chamber still has been used due to the fact, that disassembling would be too time consuming. There was no overpressure applied during the trials, in fact the chamber was kept open to decrease the heat buildup and its negative effects on the cord. Because the evaporation of water was very reliable, the flow heater was capable to run higher throughputs than the 150 g/h maximum used with other precursors.

The dip with which the samples described in Table 15 and Table 16 were treated, had the following recipe:

95 ml	Ethanol
5 ml	H_2O
5 w%	TESPT
2 w%	Acetic acid

This solution was stirred for 2 hours before usage.

The series of experiments discussed in this section were done with the following plasma treatment settings:

Plasma power setting:	S1 (see Table 1)
Cord speed:	10 m/min
Evaporation temperature:	110 °C
Pre-drying of cord:	no

Flow rate (FR) and ionization gas (ION) were variable and are mentioned individually in Table 15, where also the results for the PET test series are listed.

Interestingly, with air as ionization gas there was no improvement over the previous TEOS trials; neither with the dipping method, nor with the incorporation method. When nitrogen gas was applied instead of compressed air, a significant improvement with the incorporation method (compound with 5 w% TESPT) was found. A jump from about 40 N to 60 N of H pullout force was measured. This is by far the highest achieved adhesion force for PET in this study. Unfortunately, at this point of the study it was decided, to focus on sulfur-containing precursors for the remaining time. That is why the nitrogen treated H_2O coated cord was not tested anymore with a dipping process. Answering the question, if similar or better results would have been possible with that method should be the topics of further work.

Table 15: H_2O plasma treated PET cord - adhesion data of dipped and incorporation TESPT samples.

PET	Tensile Test		H-Pullout Force [N]			Conditions	
Sample	Fmax [N]	EaB %	DIP 1	DIP 2*	Incorp.	ION	FR
H_2O	151,8	112%	42,1	40,5	40,0	Air	300
H_2O	150,0	113%	40,7	42,8	40,2	Air	400
H_2O	155,0	113%	-	-	59,8	N2	400
RFL	-	-	-	-	83,0	-	-

***) DIP 24 hours old**

The question remains, why the nitrogen gas caused such an improvement in performance. Clearly, the break down voltage of nitrogen is higher compared to air and therefore, the plasma contains more energy. As the PET is a very inert polymer, the additional energy of the nitrogen plasma very probably helped to activate the PET surface and to deposit hydroxylic groups.

Table 16: H_2O plasma treated Rayon cord - adhesion data with various TESPT incorporations.

Rayon	Tensile Test		H-Pullout Force [N]		Conditions	
Sample	Fmax [N]	EaB %	DIP	Incorp.	ION	FR
H_2O	152,5	119%	45,1	44,8	Air	300
H_2O	162,4	117%	41,5	48,8	Air	400
H_2O	160,7	116%	DoE	54,1	N2	400
RFL	-	-	-	119,3	-	-

The results for Rayon are shown in Table 16: the trend is similar to the one seen for PET. Here as well the nitrogen gas caused an improvement in adhesion.

However, the effect is less prominent, and the highest values of pullout force are lower than the ones achieved with the sulfur precursor.

The potential of this treatment was further elucidated in a DoE setup (see Chapter 4) for the nitrogen/H_2O treated cord. The DoE focused on the dip properties and was carried out with the following parameters:

- A = Water content;
- B = TESPT/Acid content;
- C = Temperature/Time.

The actual plus and minus settings were set to these values:

A+ = 9 ml	A- = 1,8 ml;
B+ = 4,35 ml TESPT, 4 ml Acid Acid;	B- = 0,87 ml TESPT, 1 ml
C+ = 120ºC, 2 minutes	C- = 60ºC, 120 min.

For simplicity reasons, the TESPT content and the amount of acid were coupled together as well as temperature and time. While that leaves room for further studies, the carried-out DoE could deliver interesting results. These are gathered in Table 17 below.

Table 17: DoE trial with Rayon cord - Results overview.

DoE [A/B/C]	H-Pullout Force [N] x	s	v
CP	54,5	7,9	14,4
+++	70,2	6,0	8,6
+−+	63,7	5,3	7,9
−++	66,8	6,6	10,4
−−+	66,0	6,2	9,4
++−	60,8	4,2	6,9
+−−	62,0	6,4	10,4
−+−	55,8	4,8	8,6
−−−	59,9	5,3	8,9

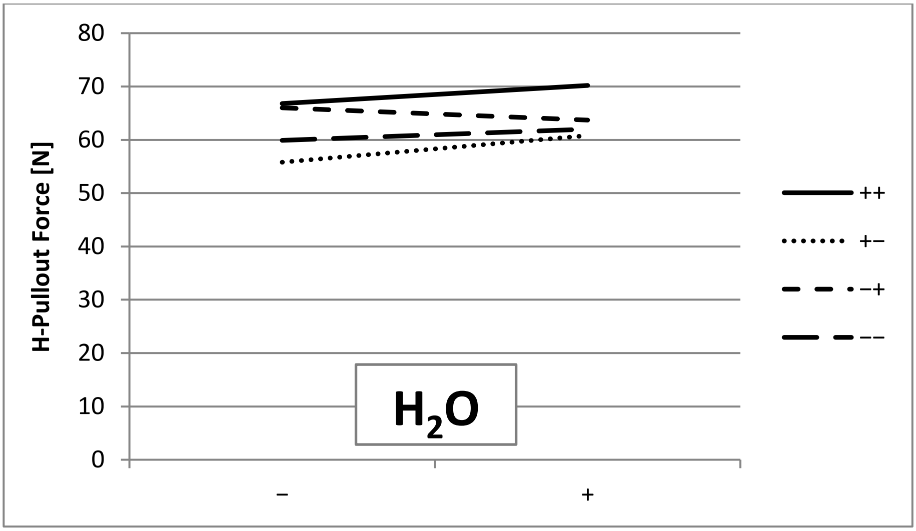


Figure 80: DoE data - Effect of water content in the dip on the adhesion.

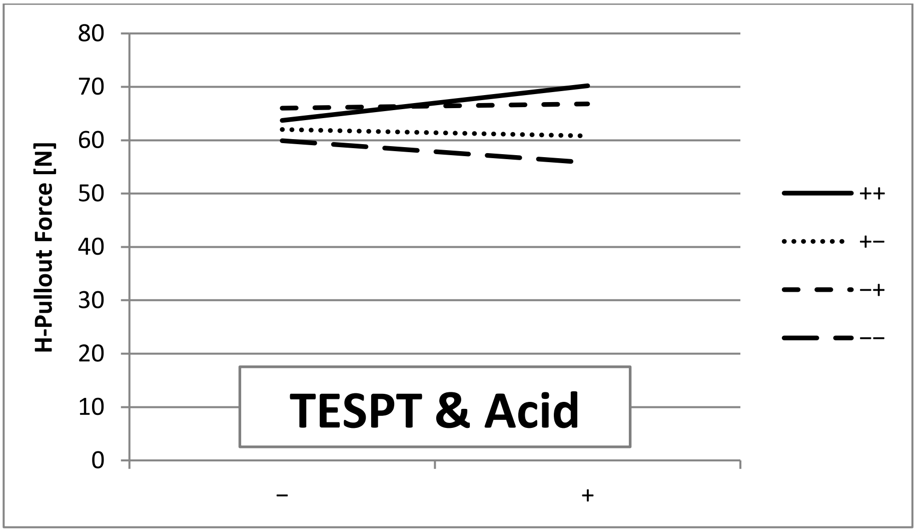


Figure 81: DoE data - Effect of TESPT and acid content in dip on adhesion.

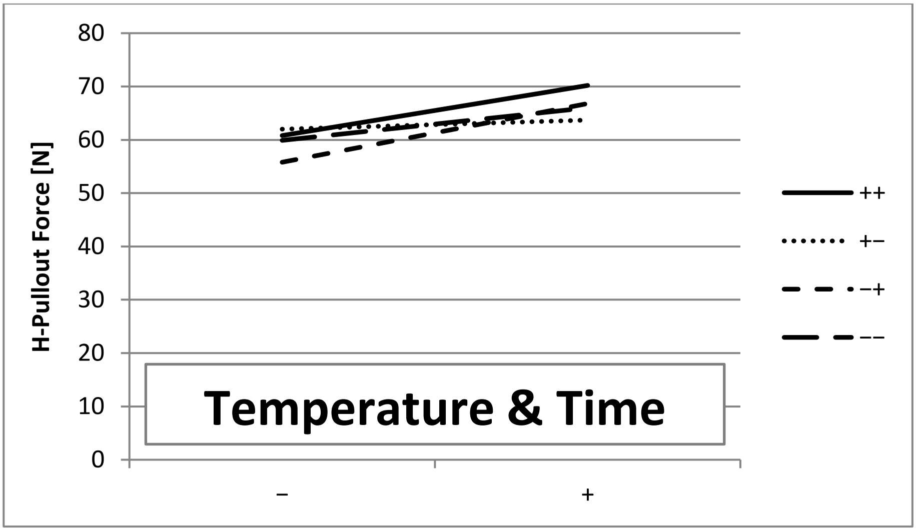


Figure 82: DoE data - Effect of temperature and time on adhesion.

Figures 80 to 82 feature each one parameter of the DoE trial to highlight the effect it has on the other parameters in each possible configuration. Before those figures are discussed in detail, it is worth mentioning, that the center point (CP) listed in **Table 17**, has the lowest adhesion values of all configurations. Even though the standard deviation is relatively high, which is common for H-pullout tests, this is remarkable.

In Figure 80 the amount of water in the dip solution and its effect is shown. The samples with a plus of TESPT benefit from additional water in the dip, while those with less TESPT show no affection. This is not surprising, as a higher amount of TESPT consequently requires more OH groups for silanisation. If more TESPT is present, it will benefit from more OH groups independent from the temperature setting. Less OH groups are less harmful at low temperatures. When the temperature is high, less OH groups hinder the silanisation reaction as they decrease its reaction speed and therefore decrease the adhesion.

Figure 81 shows the effect of TESPT and acetic acid on the silanisation process. It mainly contributes to the adhesion, if enough OH groups and heat are available (++ sample). Otherwise it has no or even a negative influence (-- sample) on the performance.

Finally, temperature and time effects are shown in Figure 82. Clearly, higher temperatures, namely 120 °C, in a shorter time interval (2 min) are more efficient than lower temperatures (60 °C) during a longer interval (120 min). The samples with more TESPT benefit the most from the elevated temperatures, but the trend is overall positive.

Looking at the results, another DoE with the +++ settings as CP would be a good starting point to further determine where the optimum is located. In another step the effect of temperature, TESPT as well as acetic acid alone should be investigated in more detail. The results of this DoE showed clearly, that the technology has potential and further optimization could lead to competitive adhesion values. This holds true for PET, which probably would benefit strongly from the results of this Rayon-DoE already.

5.5 CONCLUSION

Overall, it became clear in this study that this way of adhesion promotion is very promising and that it has potential to replace the conventional method of RFL coating. The initial precursor turned out to be not the optimal one, as TEOS was unable to form the required functional groups to react with the coupling agents in the plasma. But with demineralized water, which has many advantages like no toxicity, ease of handling, no environmental burden, etc., a novel route was taken. This technology unveiled the best PET adhesion values reached with plasma treatment, and the DoE test series showed which parameters are the ones to bring Rayon cord to a satisfactory level as well. However, the RFL cords still show the highest adhesion values.

A disadvantage of this technique is, that it requires further processing after the plasma treatment to incorporate a coupling agent. Unfortunately, the coupling agents in a silica compound have already reacted when the cord-rubber bond is made; it cannot react anymore with the cord surface. Therefore, a separate cord silanisation step is mandatory.

CHAPTER 6

The Cord-Rubber-Interface Structure

In the present chapter, the interface between the two materials, rubber and cord, is investigated. This interface is the zone, in which adhesion phenomena and the force transmission take place. Therefore, it is important to gain more insight into the specific structure of the interface and to understand how the adhesion promoting systems affect it.

Main factors in this respect are chemical moieties on the surface of the cord that can react with the elastomer during curing. Besides, filaments on the surface of the cord can form mechanical bonds. Penetration of the rubber into the cord structure is a crucial factor, next to a gradual transition of the modulus from the cord to the rubber. These adhesion mechanisms will be discussed in this chapter.

6.1 INTRODUCTION

The interface between both materials is the determining zone where the adhesion phenomena and the force transmission take place. With the general problem statement of this work in mind, as described in Chapter 2, the adhesion phenomena between the fiber or cord and the rubber is a crucial part that needs to be understood.

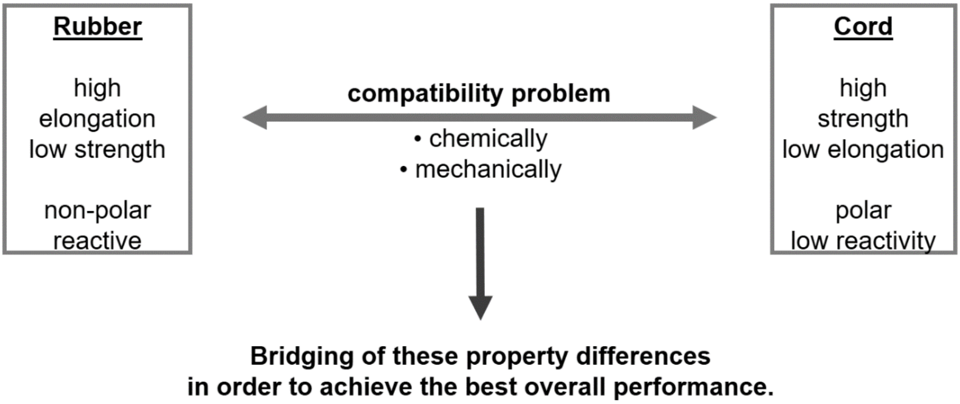


Figure 83: The general problem statement highlights the particular role that the interface has when it comes to adhesion promotion and force transmission.

The interface is the only interaction area, in which adhesion can be build up; it is the transition zone that chemically and mechanically bridges the property differences of both materials. Within this chapter, a comparative study of cords treated with RFL and the thiophene plasma coated cords, both embedded in rubber, by microscopic methods is performed. Differences in cord surface structure and cohesive or adhesive failure, which were observed while testing the mechanical properties of the cord-rubber composites, can be partly explained after visual inspection. Furthermore, the influences of rubber temperature and pressure on the cord surface penetration and therefore on adhesion are studied by laser scanning confocal microscopy. Derived from these observations, a theory is developed that explains the observed phenomena and links the mechanical properties to the results of the microscopic study. To elucidate a possible chemical bond from the cord to the rubber, the amount of sulfur on the cord surface is measured by a carbon/sulfur analyzer, and the data are put in correlation with the adhesion values. Conclusively, the data and observations of this chapter are combined and related to the outcome of the previous chapters to create a summary picture.

6.2 DIFFERENCES BETWEEN THE RFL AND PLASMA COATED RUBBER-CORD-INTERFACES

Even for the untrained eye, the differences between the Rayon cord-rubber interface of RFL or the plasma treated cords are clearly noticeable, when looking at microscopic pictures of cross-section cuts, as shown in Figure 84. The RFL treated cord (left) had the typical orange color of the dipping solution, while the plasma treated (thiophene coated) cord (right) kept the original color of the Rayon cord. The orange color is visible throughout the whole cord structure, which is evidence that the RFL dip penetrates the cord structure to the core and is present on the surface of all filaments. There is a concentration gradient from the outside to the inside of the cord, visible as a dark orange outer ring and a lighter colored inner part. Close to the interface with the rubber, the interaction with the rubber is visible as a thin dark shell around the cord. The dip forms a closed surface around the cord filaments, it therefore acts as an intermediate between rubber and cord.

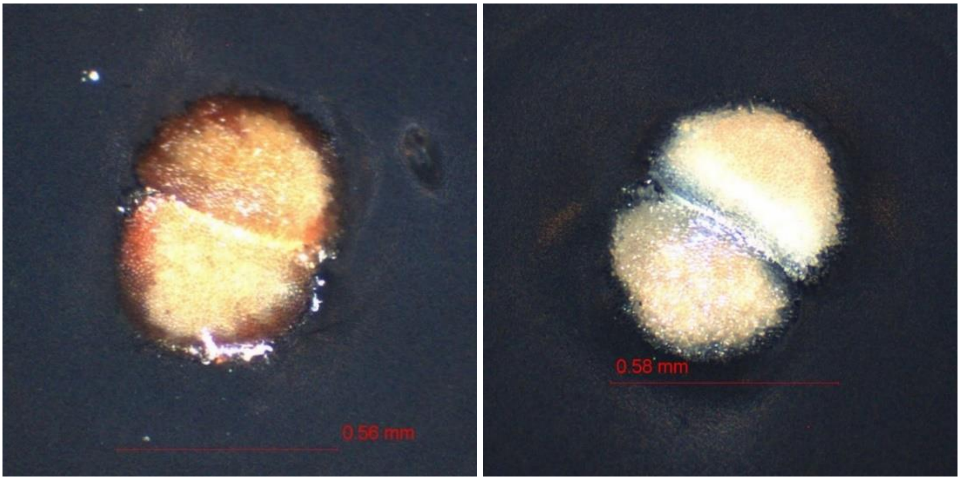


Figure 84: Microscopic pictures of the cross-sections of a RFL treated cord (left) and a plasma thiophene coated cord (right).

This contrasts with the plasma treated cord, where an interaction only with the outer filament layers is visible: the rubber penetration is clearly less than from the RFL-dipping, as it only affects the filaments close to the interface, not the deeper layers. This could be expected, as the RFL-dip has a low viscosity that is optimized to penetrate the cord, while the viscosity of the rubber compound is much higher. In the case of plasma treatment, the picture gets more complex, when the plasma deposited layer is considered as well. Unlike the rubber, the fragmented precursor molecules in the plasma have a much higher chance to penetrate in the cord, as they are much smaller than the molecules contained in a RFL dip. But as they probably react in the first contact position, it is not certain if active molecule fragments can reach and cover areas which lay much deeper in the cord structure. Therefore, even if the rubber can penetrate the cord up to several layers, it remains doubtful, if the rubber molecules then can interact with the cord surface.

Figure 85: Rubber cords pulled out of a rubber block. The RFL treated cord is shown on the left-hand side and plasma treated cord on the right-hand side.

Another difference between RFL and plasma treatment is illustrated in Figure 85. The RFL-dip causes a better rubber-cord bond, therefore the load is more evenly distributed over all the single filaments of the cord. Consequently, the place of failure is mainly in the rubber, visible by the coverage of the cord by large rubber blocks: cohesive failure. Only a few filaments are separated from the cord, which means that the force peak is usually below the force that a single filament can withstand. This can be seen by the counterpart of the H-test sample as shown in Figure 86, where only a few filaments stick to the rubber. On the right-hand side of both figures, the plasma treated cord is shown. The cord looks much more damaged after the adhesion test: many filaments stick out of the surface and only a small part of the cord surface is covered with rubber after the H-test, indicating mainly adhesive breakage. Consequently, in the counterpart many filaments are visible, which were torn out of the cord by the force of the applied mechanical stress. This failure mode indicates, that indeed the force was not distributed well enough within the interface between cord and rubber, and that the force was too high for the single filaments within the cord. The weakest spot in this system is within the cord: the filaments are not held together by the penetrating polymer in the case of plasma treatment, and therefore the filaments are pulled out of the composite. This is an indication that the adhesion between rubber and outer filaments is high, as otherwise no filaments would stick to the rubber matrix. Therefore, a better force distribution is required for enhanced pullout forces.

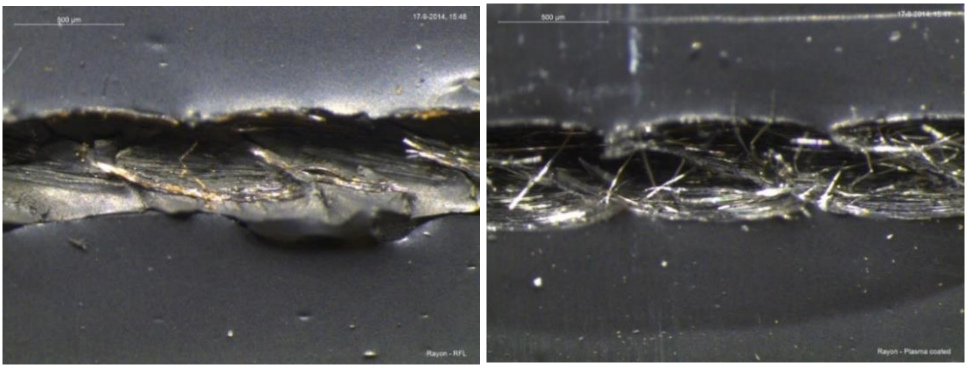


Figure 86: Counterpart of the pulled-out cords shown in Figure 3; RFL treated cord on the left-hand side and plasma treated cord on the right-hand side.

Closely observing the samples after performing a SPAF test (see Chapter 4) with an optical microscope supported the conclusions drawn from the H-pullout samples analysis. At both, RFL and plasma treated cords, rubber still covers wide areas of the cord. A certain pattern is visible unveiling areas where the rubber is peeled off from the cord and only some traces are left. The RFL dipped Rayon cord exhibits some isolated filaments in those areas: see Figure 86, but the filaments are well bundled with the rest of the cord due to the dip. This contrasts with the plasma treated cord, where the overall pattern: see Figure 87 (RFL) and Figure 88 (plasma), resembles the one of the RFL treated cords, but when the focus is set on the individual filaments, differences in the interface structure become obvious. While the coverage with rubber is sufficient: Figure 89, it is clearly visible that the filaments interact more individually with the rubber. That is in line with the conclusions from the H-pullout test samples. The filaments do not form a unified interface like RFL does, which is shown in an idealized manner in Figure 90.

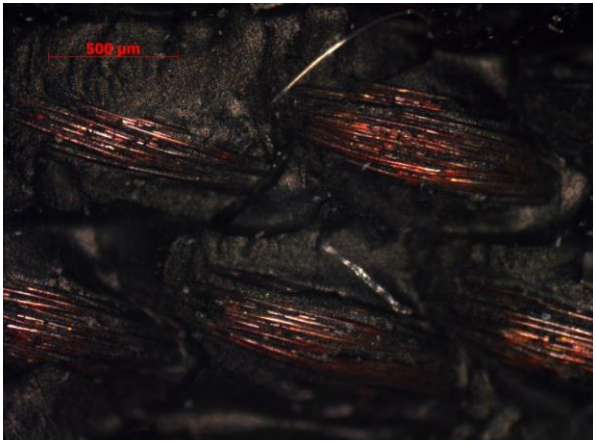


Figure 87: RFL-Rayon cord embedded in rubber after a SPAF test.

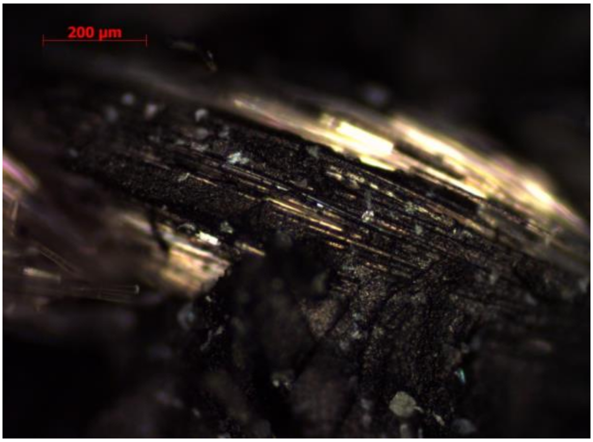


Figure 88: Thiophene plasma coated cord after a SPAF test.

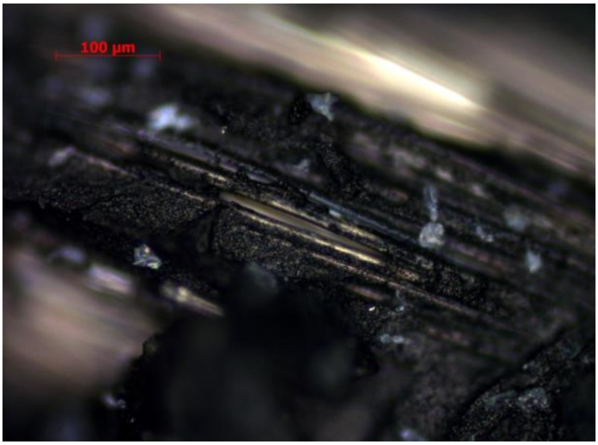


Figure 89: Thiophene plasma coated cord after a SPAF test.

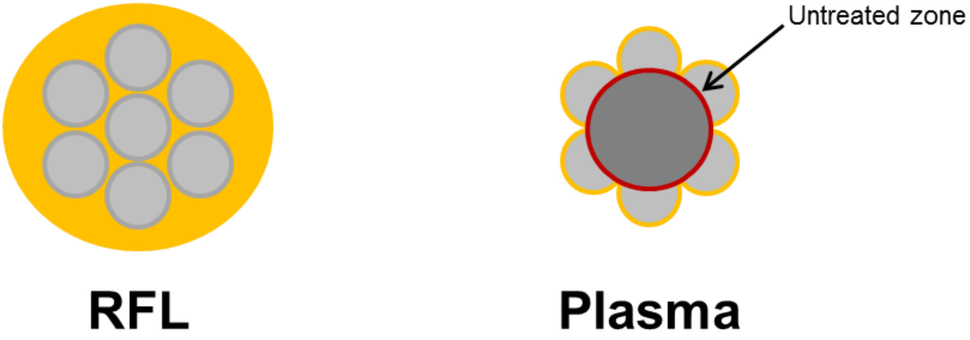


Figure 90: Idealized scheme of the different interfaces that are interacting with the rubber matrix. The yellow color represents the dipping/coating and the grey circles symbolize the filaments of the cord.

Besides this difference of the interface covering all single filaments and acting as a unified one (RFL) or covering only the outer surface and forming individual shells around filaments (thiophene plasma), there is another significant difference which affects the adhesion to rubber. This is the modulus transition from the high-modulus cord material to the highly elastic rubber. In case of plasma treatment, that transition is very abrupt, as the plasma coated layer is very thin: in fact, the change of modulus is a question of nanometers for a plasma coated cord.

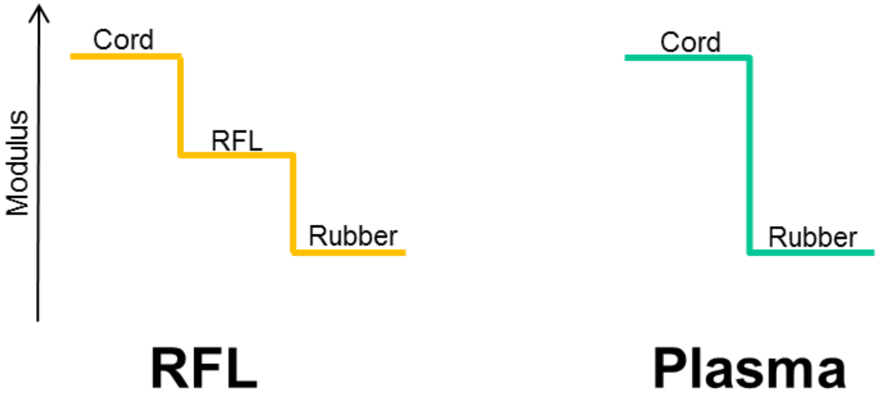


Figure 91: Difference in modulus transition between both adhesion promotion techniques.

The RFL dipped cord has an intermediate modulus in the transition layer due to the rubber content in the dip, which mediates between the extremely high modulus of the cord and the significantly lower one of the rubber. Not only is the dip simply thicker than the plasma coating, it is also interacting in multiple layers with several filaments of the cords. This is one of the reasons for the higher overall adhesion. While both systems can form chemical bonds between both materials, the RFL-dip incorporates more filaments within a larger depth having an intermediate modulus. Plasma coating is limited to a small penetration depth on the cord surface. This enables the RFL-dip to distribute the force gradually between more filaments than in the case of a plasma coating.

The problem for this alternative adhesion promotion technique is, that it is competing in an environment which has been developed for the RFL-dip technology: the RFL dip has been an industrial standard for decades, and compounding, processing and measuring are adjusted to this adhesion system. This also includes the twist of the cord, which is optimized for the RFL treatment. However, this might not be the optimal structure of the cord for the plasma treatment. A higher twist might be favorable for the latter technology: each individual filament will then appear on the cord surface for a shorter distance, but at higher frequencies. In such a way, the number of filaments which can be reached by the plasma-modification as well as the rubberizing would be increased, giving the cord a more unified structure. That in combination with a better understanding of the chemical composition of the plasma deposited polymer will help to significantly enhance the adhesion performance of a plasma treated reinforcing cord.

6.3 IMPROVEMENT OF PENETRATION DEPTH

A higher penetration depth of the cord by the rubber is a crucial prerequisite for good overall adhesion performance. From the microscopic study, the main concern was that the penetration depth is not sufficient and that therefore not enough filaments are contributing to the adhesion force. However, if the penetration is too deep, a loss in dynamic properties occurs. It is accepted that the best adhesion performance is achieved with about four layers of filaments involved. That information was shared by Teijin Aramid Fibers during a technical meeting.

If the penetration is to deep, a loss in dynamic properties occurs. After plasma treatment and rubberizing, the penetration depth under standard curing conditions is found to be insufficient. The dominant processing parameter to achieve a certain penetration depth is the pressure with which the rubber is transferred into the cord structure. To study the effect of the applied pressure during processing and vulcanization on adhesion, the following two series of experiments were carried out:

- Different pressure and temperature conditions in the cross-head of the extruder;
- Variation of the vulcanization pressure in the press.

The above parameters are expected to give control over the penetration of the cord. One of them should be dominant for the achieved penetration depth. To understand which of the parameters this is, a comparative test was carried out. In this test series, three differently treated Rayon cords were vulcanized under three different vulcanization pressures. This approach should unveil the effect of vulcanization pressure. The results are shown in Figure 92.

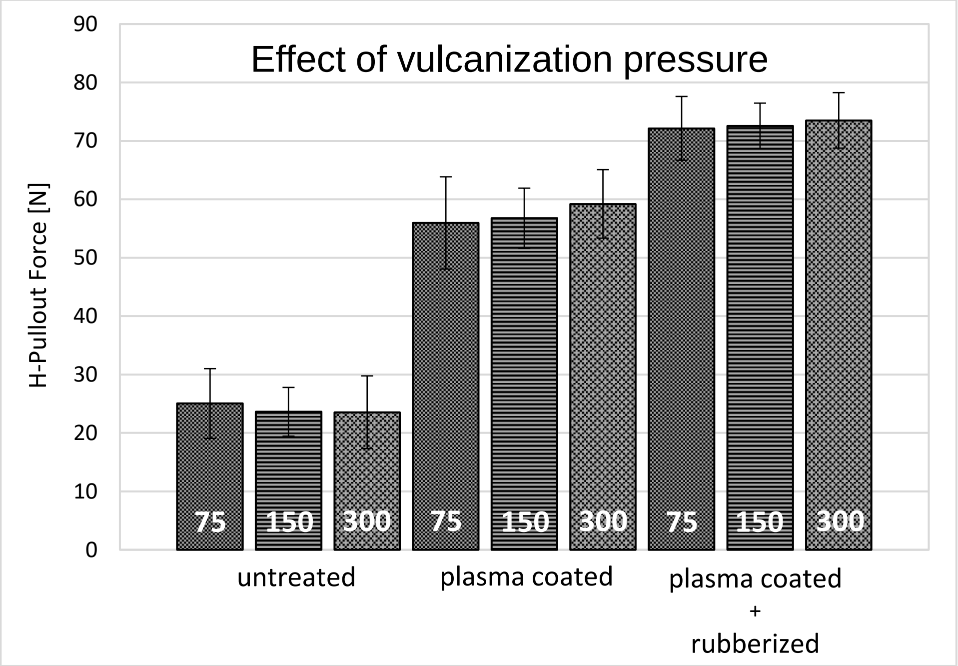


Figure 92: Samples exposed to different closing pressures of the vulcanization press. The numbers represent the pressures in bar during vulcanization.

The differences in cord treatment are as follows: an untreated raw Rayon cord, a thiophene plasma coated and a rubberized thiophene plasma coated cord were used in this comparison. The samples were cured at 160 °C for 30 minutes and the closing pressure was varied between 75 and 300 bar. Based on the H-pullout values, the samples can be separated into three groups, which are determined by the cord treatment and not by the vulcanization pressure. This is a good indication, that the vulcanization pressure does not have a major influence on the penetration depth, as the adhesion in the H-pullout test is independent from the vulcanization pressure within this range.

In the next step, a test with varied settings of the cross-head extruder was performed with constant plasma treatment conditions. The concept aims for a control of the viscosity of the rubber compound, mainly via the extruder screw speed: a higher screw speed causes more friction and, therefore, generates more heat in the rubber compound. Two screw speeds were chosen: 20 and 100 RPM. These speeds lead to temperatures of 100 and 110 °C in the rubber compound, respectively. With the bypass in the extruder head the pressure conditions were controlled. The pressure was in the range of 75 to 280 bar. An overview of the settings can be seen in Table 18. The table also features a value for the penetration depth. This value is based on the average depth (in layers of filaments) that the rubber has reached and is taken from at least 3 different microscopic images of the same sample.

Table 18: Settings and results of the extruder experiment

Sample	Extruder settings			Penetration	H-Pullout		
#	T [°C]	RPM	p [bar]	Depth*	F_{max} [N]	s	v
1	100	20	75	2,3	74,5	3,69	4,96
2	100	20	110	1,7	77,3	2,61	3,37
3	110	100	110	3,5	77,7	3,63	4,68
4	110	100	280	2,5	73,6	4,59	6,24

***) Value represents the average penetration depth in layers of filaments of the cord.**

While there are significant differences in pressure and screw speed as well as in temperature (and therefore in viscosity), the results measured with the H-pullout test are very similar. On the one hand, sample 3 with a temperature of 110 °C and a screw speed of 100 RPM and the bypass open (relatively low pressure) reached the best penetration depth and achieved the best H-pullout values. On the other hand, sample 2 reached nearly the same H-pullout value with the lower rubber temperature and extruder screw speed plus closed bypass. Both had the same pressure due to equal bypass settings. However, the penetration depth of sample 3, where the rubber is assumed to have a significantly lower viscosity because of the processing temperature, is indeed much higher – 3 to 4 layers – compared to sample 2, in which the penetration depth did not get deeper than 2 layers: see the laser microscope images of sample 2 and 3 in Figure 94 and Figure 95 in comparison with Figures 11 and 14. Unexpectedly, sample 4 with the highest pressure of 280 bar does not have a better rubber penetration. This clearly indicates, that sample 3 has the best compromise of temperature, screw speed and pressure inside the head. Apparently, a higher pressure in the crosshead compresses the cord and prevents the rubber from penetrating the cord between its filaments. Besides, a pressure variation in the crosshead when the bypass is open, might as well result in too low pressures at certain positions in the crosshead, and as a consequence, a low degree of interaction between cord and rubber.

As a conclusion, it is possible to enhance the rubber penetration of the cord with the extruder settings, but this does not improve the H-pullout force. Based on the technical information from Teijin, the penetration of sample 3 should be close to optimal. Enough filaments are involved in the process of transferring the load from the rubber to the cord. However, this did not result in a higher cord-rubber bond strength measured in the H-pullout test. This indicates that another limitation must be responsible for the low adhesion values compared to RFL treated cords. If the plasma coating does not penetrate below the cord surface, a deeper penetration depth of the rubber is potentially contra-productive, as the adhering outer filaments are more isolated from the cord core. Figure 97 is showing a potential failure mode, which can be derived from the paragraph above. It can be seen, that those filaments which are attached to the rubber do separate from the actual core of the cord, in which the filaments are not attached to the rubber. If that is the case, the detached filaments cannot transfer the given load to other filaments of the cord and this transition zone between attached and not-attached filaments becomes the weakest point. A distributed transmission of the applied stress over this transition zone is not possible. The stress for the attached individual filaments reaches a level, which ultimately causes failure; first at the single filament, but in a chain reaction for the whole cord as well. In such a scenario, not the established adhesion between cord and rubber, but the unbalanced stress distribution causes the failure. A cord that alternates the filaments more frequently from the inside to the outside, in fact a cord which has a higher twisting, should be able to accept higher stress levels. A higher twist ensures that all filaments are more often and for a short distance on the cord surface. Therefore, the force distribution would be better as more filaments interact directly with the rubber.

Overall, the penetration depth should be around 4 layers deep for optimal adhesion results. However, in the case of plasma treatment the penetration depth has less impact on the adhesion compared to the RFL treatment system. The reason is the limited penetration depth of the actual plasma treatment. Even if the rubber penetrates deep enough into the cord structure, the filaments below the surface are probably not covered by the plasma coating and are therefore passive towards the rubber. If more filaments are on the cord surface for a shorter distance, as explained above, the force distribution is more balanced for the plasma treated cords.

Figure 93: Sample 1 (rubber compound temperature: 100 °C, pressure: 75 bar) has a penetration depth of 2,3.

Figure 94: Sample 2 (rubber compound temperature: 100 °C, pressure: 110 bar) has a penetration depth of 1,7.

Figure 95: Sample 3 (rubber compound temperature: 110 °C, pressure: 110 bar) has a penetration depth of 3,5.

Figure 96: Sample 4 (rubber compound temperature: 110 °C, pressure: 280 bar) has a penetration depth of 2,5.

Figure 97: Possible failure mechanism: the filaments attached to the rubber get separated from the core.

6.4 ANALYZING THE EFFICIENCY OF THE PLASMA COATING

In Chapter 4, a clear difference between the adhesion promotion technologies was seen. To better understand how the plasma coating is affecting the interface, the amount of actual sulfur on a given cord sample was measured. For the samples with a thiophene coating this could be an indication of the amount of deposited plasma polymer. As reported in Chapter 4, it is very difficult to analyze the surface of the cords. Several methods were finally unable to show a difference between a reference cord and the plasma treated samples. Another approach was now done by using a carbon/sulfur analyzer. The cord samples were analyzed by Nokian Tyres (Finland).

The amount of sulfur was determined using a ELTRA CS 500-carbon/sulfur-analyzer, which is shown in Figure 98. The analyzer operates as follows: the samples are burnt in an oxygen atmosphere and the combustion gases are analyzed by infrared absorption. During the combustion, the sulfur within the sample is oxidized to SO_2 at combustion temperatures as high as 1350 °C to 1450 °C. The signal given by the infrared analyzer is selective and corresponds to the concentration of the gaseous mixture. In the beginning, the sulfur analyzer is checked by a calibration measurement with a substance that has a known sulfur content. In this analysis, approximately 150 mg of the calibration substance was weighed. Afterwards, the samples with approximately the same weight are analyzed. The given result is then expressed in mass-percentage (m-%) of sulfur.

Figure 98: ELTRA CS 500 carbon/sulfur-analyzer.

The results of the measurements are shown in Figure 99. The first three bars on the left-hand side are Rayon samples, where the effect of thiophene as precursor is analyzed. Clearly, the amount of sulfur does not significantly change and remains on a low level. Thiophene as molecule has the composition C_4H_4S, which is equal to a molecular mass of 84 u, where 32 u is the atomic mass of sulfur. The rayon cord used in the project had 1840 dtex, which means that 10 m of cord have a weight of 1,84 g. The thiophene flow rates in those trials were 300 and 150 g/h, respectively. This in fact correlates with a theoretical maximum of 5 or 2.5 g per 10 m of cord. Looking at the molecular mass ratio of thiophene/sulfur, a theoretical maximum of 28,2 mg of sulfur should be found by the analyzer in case of a flow rate of 300 g/h and a sample weight of 150 mg. This would result in a value of 18,8 m-%. However, for Rayon the measured maximum values were below 0,1 m-%. This indicates clearly, that the efficiency of the deposition process is very low. The same calculation can be made for PET too, where a similar trend is visible. The actual numbers are even lower for PET, because the cord contains no sulfur atoms, unlike rayon cord does due to its half-synthetic nature.

However, as the cord moves through the combined center of two atmospheric pressure plasma jets, it is fully exposed to the actual deposition from the plasma process; such a low efficiency is therefore not very probable. Neither the sulfur analyzer method nor the XPS measurements described in Chapter 4 could show a notable change in the chemical composition of the cord surface. Which again is very surprising when looking at the massive impact the treatment has on the mechanical properties, see Chapter 4. With an assumed efficiency of 1 % at a flow rate of 300 g/h, it can be calculated that the analyzer should find a concentration of about 2,73 m-% of sulfur for such a sample. The measured values are lower by a factor of 50. From these measurements, it is doubtful, if sulfur plays a key role in the reaction between cord, deposited coating and rubber. However, when comparing the precursors in Chapter 4, it was seen that thiophene had a much stronger effect on the adhesion strength than the similarly structured but sulfur less pyrrole. This proves that the sulfur atom is indeed playing a vital role for the reaction pattern, even though the concentration, according to these measurements, is rather low.

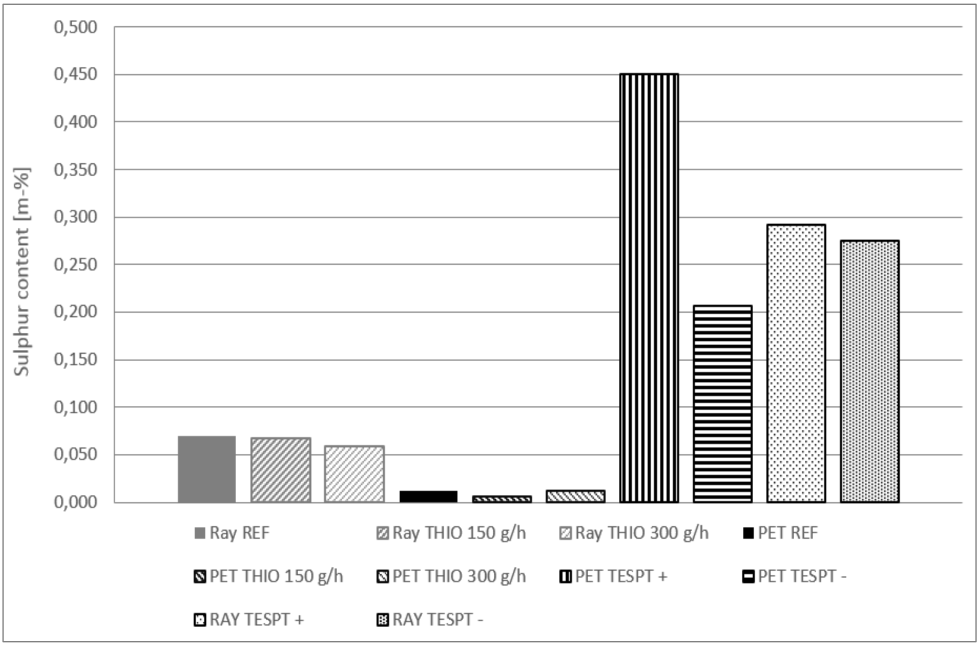


Figure 99: Overview of the sulfur analyzer results. The 6 samples starting from the left-hand side are the ones plasma treated with thiophene, the first 3 for Rayon, the other 3 for PET. In both cases a reference is compared to 150 and 300 g/h of thiophene coating. The four samples on the right-hand side are TESPT dipped samples from the DoE trials of Chapter 5.

In case of the TESPT treatment of PET, see the four samples on the right-hand side of **Figure 99** (the treatment is explained in Chapter 5) there is indeed a trend noticeable between the samples. Clearly, the amount of sulfur is for all samples significantly higher than the corresponding reference samples (Ray REF and PET REF on the left-hand side). Interestingly, the PET sample that gave the best adhesion results, H_2O plasma treatment and TESPT dipping, has also here the highest dosage of sulfur (PET TESPT+). This proves, that a dipping bath with more TESPT causes effectively more sulfur moieties on the cord surface. This means that more TESPT was deposited on the cord surface, and the higher adhesion forces show the positive effect hereof. Ergo, the H_2O plasma treatment creates a enough hydroxyl groups on the cord surface with the given plasma treatment. It is possible, that an even higher amount of TESPT in the dip will further increase the adhesion, up to a point where all hydroxyl groups are used.

In comparison with rayon, PET can attract significantly more TESPT under identical dipping conditions (TESPT+). Interestingly, the picture turns opposite when a lower concentration of dip is applied (TESPT-), where Rayon attracts more TESPT. The results of the ‘+’ setting indicate that the plasma treatment with H_2O as precursor is more effective for the PET cord than for rayon, as the PET absorbs a higher amount of TESPT. In Chapter 5 we have seen, that the plasma coated PET cord can attract more TESPT from the dip than the just cleaned cord. Therefore, independent of the TESPT concentration in the dip, the PET cord is clearly able to interact better with the TESPT than the rayon cord after H_2O plasma treatment. This is an encouraging result of the plasma treatment, as in general PET is clearly less responsive than rayon. That raises the question, why the lower TESPT concentration (TESPT-) shows a lower result for PET than for rayon? An at least equal amount of sulfur concentration would have been expected for the case, that both cords utilized the full amount of TESPT (-). One explanation might be, that the concentrations of TESPT for each TESPT dipping process where not the same for PET and rayon, even though the dip formulations was identical.

The conclusions of the sulfur analyzer measurements within the present chapter are:

- -that a H_2O plasma treatment is proven to be effective, and besides relatively environmentally-friendly;
- - that H_2O plasma treatment can even activate the highly inert PET cord surface.

However, based on these results the amount of deposited thiophene is clearly much lower than expected. While the thiophene plasma coating of rayon gives indeed good adhesion results, the efficiency of the plasma treatment in terms of the ratio of injected and deposited precursor needs to be improved to let this technique become interesting for industrial applications, in view of the large mass loss in the present configuration.

6.5 CONCLUSIONS AND OUTLOOK

Within this study, different structural aspects influencing the adhesion strength of rubber on cord are studied and optimized. The penetration depth of rubber into cords is one of the crucial parameters for good adhesion. However, the general statement that a penetration depth of 4 filament-layers could not be confirmed: it did not give the expected high adhesion level.

The pressure exerted in the extruder head when rubberizing the cord after the plasma treatment was expected to have a considerable influence on the penetration depth. However, in actual practice there is no direct correlation between extruder pressure, penetration depth and adhesion: the highest pressure did not lead to best penetration nor adhesion. Explanations for this effect might be, that a high pressure in the crosshead compresses the cord too much, preventing a deeper penetration. Besides, there might be a pressure distribution in the crosshead when the bypass is open, resulting in insufficient pressure at certain positions in the crosshead.

With optimized extruder settings, a greater number of filaments is attached to the rubber, but the adhesion results stagnate on a certain level: an indication, that the plasma coating does not reach deeper filament layers and is indeed a pure surface treatment. A failure mechanism which might be responsible for the limitation of the adhesion strength was observed: the filaments embedded in rubber do separate from the inner part of the cord. This means, that the adhesion between these filaments and the rubber is stronger than their connection to the core of the cord.

The efficiency of the plasma coating process is also investigated. The plasma nozzles were positioned in a way, that the efficiency of the process is as high as possible. But the sulfur analyzer as well as previous XPS measurements have shown, that the deposition reached by the plasma treatment is only a minor fraction of what was injected into the chamber. Still, adhesion measurements clearly show, that the treatment itself and in particular a high precursor flow rate (and ergo higher deposition rates) do enhance the adhesion.

These results show the potential of this technique, and they also define the requirements for a further improvement of the plasma setup. The efficiency of the precursor deposition needs to be increased significantly, while at the same time the exposure to heat needs to be limited to prevent damage of the outer cord filaments. Furthermore, the plasma deposition should reach deeper filament layers and the rubber penetration has to be optimized for a better interaction.

CHAPTER 7

Short and long-term effects of plasma treatment on reinforcing cord: change of cord properties

In this chapter, the change of the properties of the reinforcing cords is studied. These changes are either caused by the exposure to the plasma itself, or due to ageing over time of the plasma-modified cord. In the former case, a chemical modification of the cord surface happens, but the plasma also puts a temperature burden on the cord material, which changes its properties. In the latter case, the time-dependency of the activation of the cord surface and of the bonding to the rubber, thus the adhesion, is studied. Therefore, instant effects on the properties are described as well as gradual changes over time due to thermal ageing.

7.1 INTRODUCTION

The research described in the prior chapters was strongly focused on the adhesion promotion between reinforcing cords and rubber by plasma treatment: the effect of plasma on the cord properties was not discussed so far. Therefore, the focus of this chapter is on the properties of the reinforcing cord and how they are affected, when the cord is stressed by external factors. One external factor is the Atmospheric-Pressure Plasma Jet (APPJ) treatment causing instant changes to the cord properties that remain as a permanent effect after the plasma treatment. Another factor is ageing over longer periods of time, measured by accelerated tests at elevated temperatures.

To better understand what happens to the cord by the instant plasma effects, samples were taken right after the adhesion promotion treatment. In case of Rayon, the cords were dried in an oven and then tested in a tensile tester. Doing so, several types of plasma treatment conditions were compared with untreated cord and the RFL reference. The overall performance, force and elongation at break as well as the force at 45 N, which is an important value for tire construction, were compared. Besides, the effect of plasma treatment on the surface energy of the cord was analyzed.

Thermal ageing in a hot-air oven was performed to get a better view at the deterioration of adhesion over time. This was done in two ways: On the one hand, vulcanized samples were aged. In fact, this is the most interesting variant as it represents the performance of the final product during its service life time. On the other hand, the cord material itself was aged prior to coating with rubber and vulcanization of the specimens. This is of interest, as the time span between plasma treatment and building-in into the final product such as a tire or conveyor belt is not known. If the activated cords will be stored before further processing, as it is the case for RFL-treated cords, it is important to know what the effect of storage will be. These tests were performed with the best plasma treatment variant for each cord type: for Rayon, a thiophene plasma coating was used; in the case of polyester (PET), a H_2O plasma modification was applied.

7.2 IMMEDIATE AND PERMANENT EFFECTS OF PLASMA TREATMENT ON POLYMERIC CORDS

7.2.1 Immediate plasma treatment effect on 2-ply rayon cord with 1840 dtex

The effect of diverse plasma treatment conditions on the inherent properties of Rayon cord were investigated by monitoring the stress-strain properties (ASTM D885) of the cord. For each condition, three different plasma winding speeds were used: 30, 15, 7.5 m/min, respectively. The plasma conditions were as follows:

a) **AIR**
Plasma generator I – Cleaning unit FG1001 (CU): Air / 276 V / 5,9 A

b) **N2**
Plasma generator I – CU: Nitrogen (N_2) / 276 V / 5,9 A

c) **NAP**
Plasma generator I – CU: Air / 281 V / 6,01A
Plasma generator II – Polymerization unit FG5001: N_2 / 271 V / 9,0 A / Freq. 19 kHz
Precursor: pyrrole (300 g/h)

Next to these test samples, three non-plasma treated samples were used for comparison. An untreated virgin cord was used to describe the reference characteristics of rayon. A dried variant from the same sample was measured as well. The drying was done in a laboratory oven for at least 2 h at 120 °C and the sample then was immediately tested. The third cord, to which the plasma samples were compared to, was an RFL-dipped cord. The results are illustrated in Figure 100.

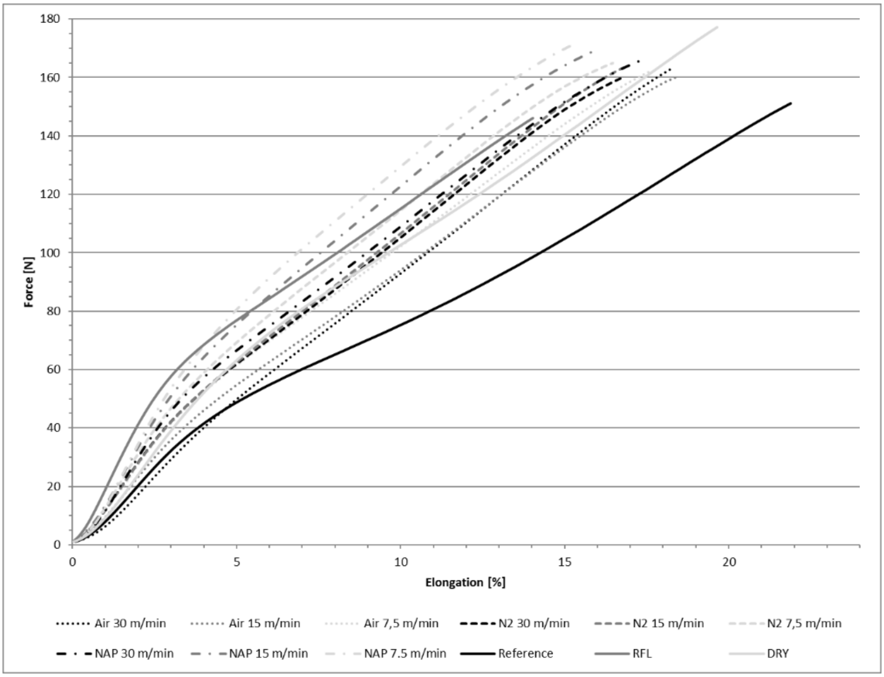


Figure 100: Tensile test (cord only) results of diversely treated rayon samples.

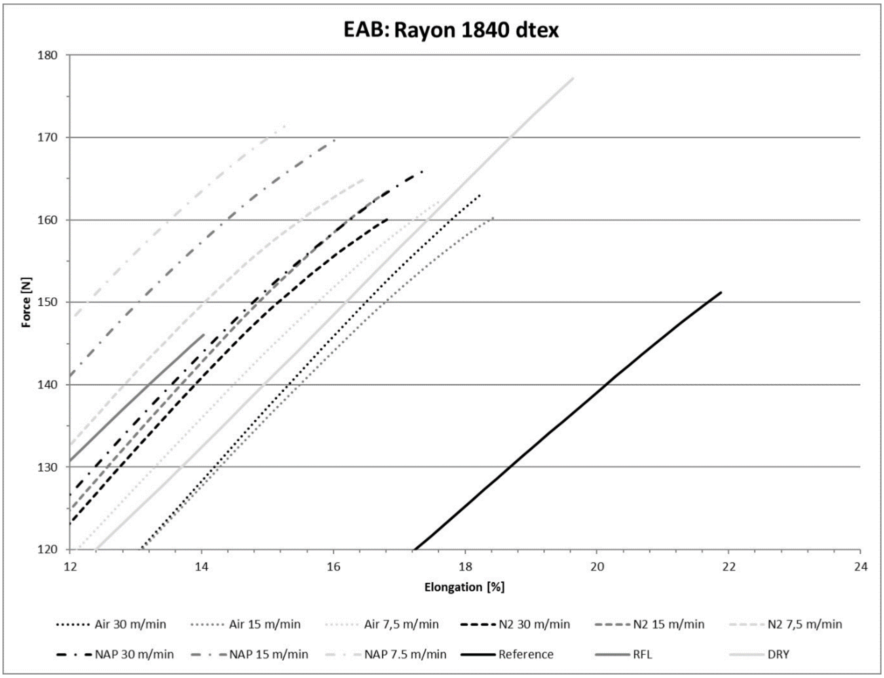


Figure 101: Close-up of the elongation at break behavior of the rayon cords.

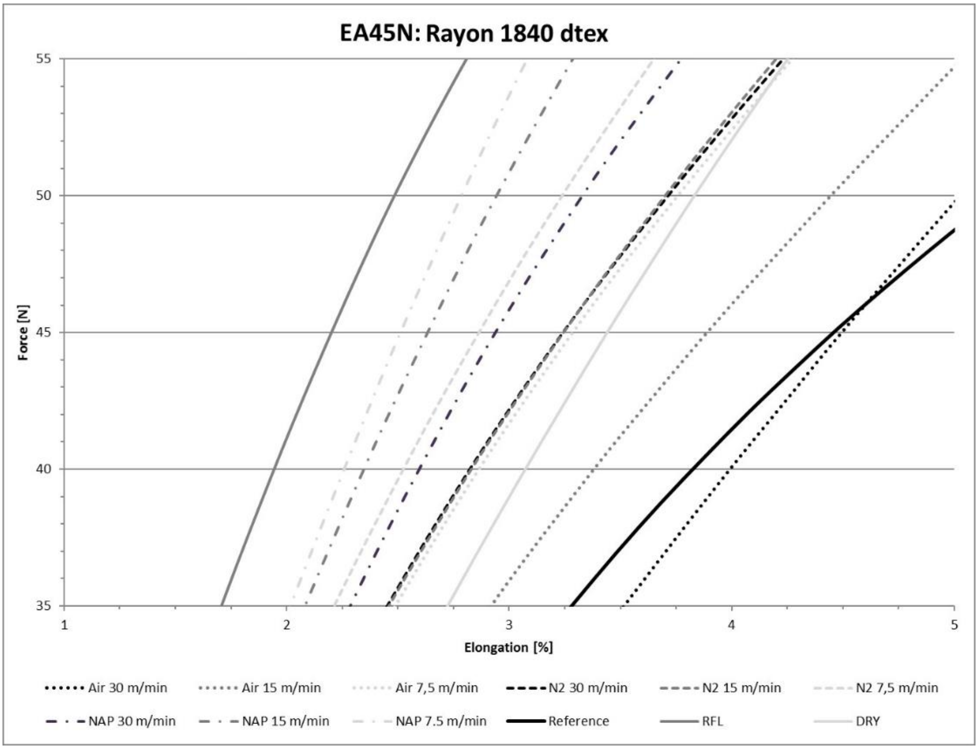


Figure 102: Illustration of the elongation at a force of 45 N.

Clearly, the RFL-dipped cord has the highest stiffness of all tested cords until a force of roughly 55 N is reached: see Figure 102. Beyond that point, the stiffness of this samples is lower compared to all other samples, and the RFL-treated sample breaks first: Figure 101. This phenomenon is caused by the fact, that until that point the RFL coating, which penetrates the cord: see Chapter 6, contributes to the cord performance. The highest strain is measured on the untreated virgin cord, which also has a rather low modulus. All treated cords show a higher stiffness, which is caused by the heat burden, that all of them received during processing. Apparently, air as ionization gas affects the cord properties less than nitrogen does. This can be explained by the higher temperatures that pure nitrogen in a plasma treatment generates compared to compressed air. The energy input from the generator was the same, as the ionization gas was changed during the experiment with a Y-valve in the gas supply section. The treatment with a precursor, in this case pyrrole, caused the largest effect on the cord properties, creating values that are close to the values of the RFL treated cord. However, that is more an effect of the second plasma treatment itself and the temperature burden than the actual precursor deposition: The degree of coating deposited by the plasma is not high enough to cause such a strong effect on the cord properties: see amount of deposition in Chapter 5. Another indicator for the temperature effect is that the impact on stiffness gets stronger the slower the winding speed is, see the shift of the EA45N curves from 30 over 25 to 7,5 m/min in Figure 3. Therefore, the duration of exposition to the plasma is a decisive parameter. The amount of deposition will increase as well with a longer residence time, but this effect has less impact than the extra temperature burden. This was also seen in the experiments, when only one plasma generator was in use without a deposition of a precursor.

The combined air/N2/pyrrole (NAP) treatment gives EA45N values closest to the RFL treated cords, and the lowest speed, thus highest treatment time, gives the best value: this again is an indication, that both treatment steps, cleaning as well as plasma polymerization, are necessary.

7.2.2 Immediate plasma treatment effect on PET-cord

Identical tests were performed with PET-cord. In this case, two different winding speeds were used: 30 and 7.5 m/min. The test was performed with the following parameters under atmospheric conditions:

a) **Air** Plasma generator I – CU FG1001: Air / 276 V / 5,9 A

b) **N2** Plasma generator I – CU FG1001: N2 / 276 V / 5,9 A

c) **NAP** Plasma generator I – CU FG1001: Air / 281 V / 6,01A
Plasma generator II – PU FG5001: N2 / 271 V / 9,0 A / Freq. 19 kHz
Precursor: pyrrole (300 g/h)

Visual inspection indicated, that the cords which were treated at a speed of 7,5 m/min showed surface defects like single filaments, which were cut and molten during the plasma treatment. At a winding speed of 30 m/min, no visual defects were found. The results for the PET cords are shown in Figure 103. Clearly, a different trend than with the Rayon cord is noticeable. The RFL coated and thus also heat-treated PET cord has a higher elongation at 45 N than the untreated cord. Overall, the material requires less force to reach a certain elongation due to the RFL coating procedure. The force at break is with 140 N about 20 N less than the reference PET cord, while the strain at break of both cords is about the same with approximately 14

%. The intense heat to which the cord is exposed by the plasma causes a decomposition effect if the cord is in the plasma zone for a too long period, thus at slow winding speeds. This can be seen by those samples that run with a winding speed of 7.5 m/min. Independent from the ionization gas, the cord properties where deteriorated strongly by the plasma. The higher the plasma flame temperature (the nitrogen plasma is hotter than the air plasma), the stronger the deterioration effect. With the higher winding speed of 30 m/min, the effect of the N_2 plasma on the cord properties is insignificant and within the measurement tolerance. Only the air plasma at 30 m/min changes the cord properties similar like the RFL coating does. However, at a force of 45 N: Figure 104, the air plasma sample still deviates from the target value of RFL, but at higher elongations, this sample matches the RFL profile. The abbreviation “NG” in the figures below stands for the FG5001 generator, which replaced the FG1001 because that unit had a malfunction. The new generator was set to the same plasma power and the same APPJs have been used for the other trials. The performance of the samples is comparable, which can be expected because the voltage and electric current delivered by both generators are similar and therefore the plasma generated in the APPJs will behave identical.

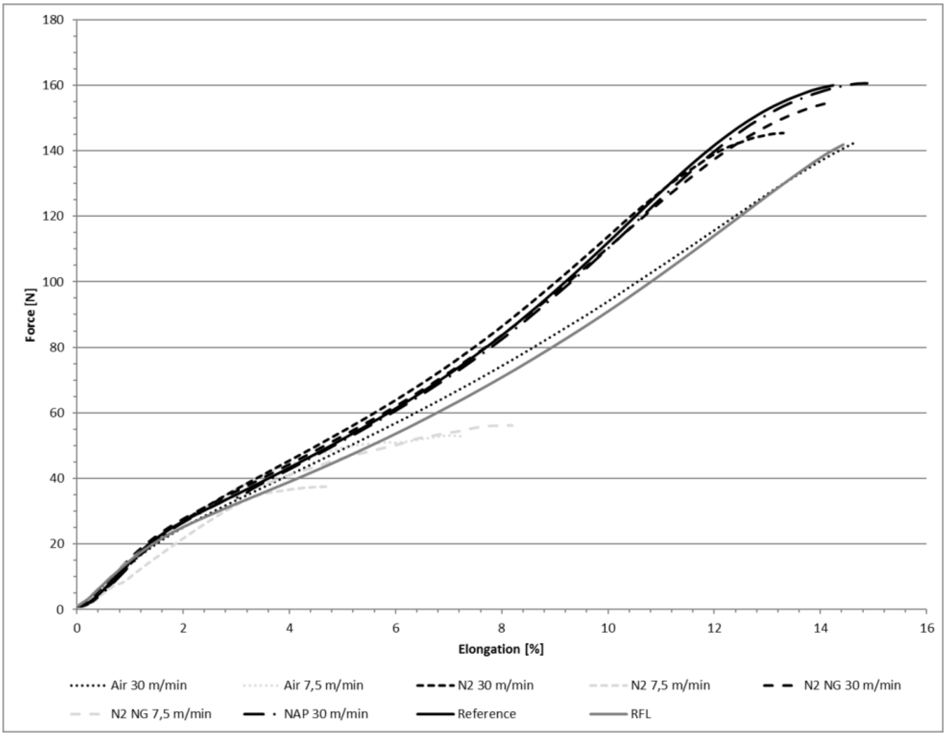


Figure 103: Plasma treatment effect on force-strain curves of PET cord.

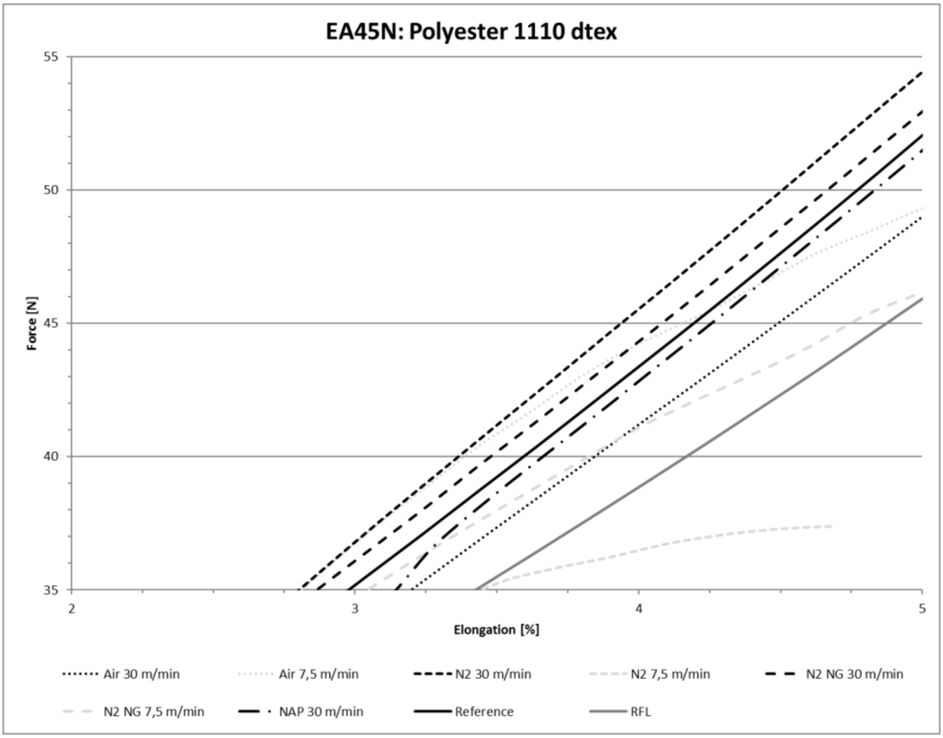


Figure 104: Close-up on the EA45N performance of PET cord.

7.2.3 Change of surface energy due to plasma treatment

The effect of plasma treatment was also measured in terms of change of surface energy using a contact angle measurement device OCA 40 Micro from DataPhysics, Germany. A dynamic sessile drop study was done to determine the advancing contact angle. Thereby, a drop of demineralized water is positioned on the cord and the initial contact angle is measured applying a high-speed camera that features a very high frame rate. The drop is then released from the feeding cannula, while the camera documents the advancing contact angle at a constant frame rate. Knowing the starting time, the frame rate allows to determine the contact angle for each frame that has been captured, thus as a function of time. The measurement ends, when the drop is fully absorbed by the cord. The measurement was repeated three times for each sample. As the permanent effect of the plasma treatment should be measured, there was a period of several days between the actual plasma treatment and the measurement of the surface angle. A measurement shortly after the plasma treatment very probably shows a different picture, but might encounter the problem of instability. The plasma settings are identical to the ones used in paragraph 7.2.1 and 7.2.2 for Rayon and PET, respectively.

Rayon experienced a strong effect by the plasma treatment on its hydrophilic character: the time to absorb the water droplet and therefore to decrease the advancing contact angle to zero was reduced significantly: see a, b, c. This effect was detectable with both plasma types, N_2 as well as H_2O. The time to reduce the advancing contact angle clearly decreases from more than 1 sec for the reference (a) to around half a second (b, c) for air and nitrogen plasma, respectively. The starting value of the advancing contact angle decreased slightly from 40˚ to about 35˚ due to the treatment, indicating as well that the hydrophilic character of rayon is increased by the plasma treatment. Besides the fact, that the effect is independent of the type of plasma ionization gas, a repetition of the plasma treatment, thus a longer treatment time, does not further increase the effect.

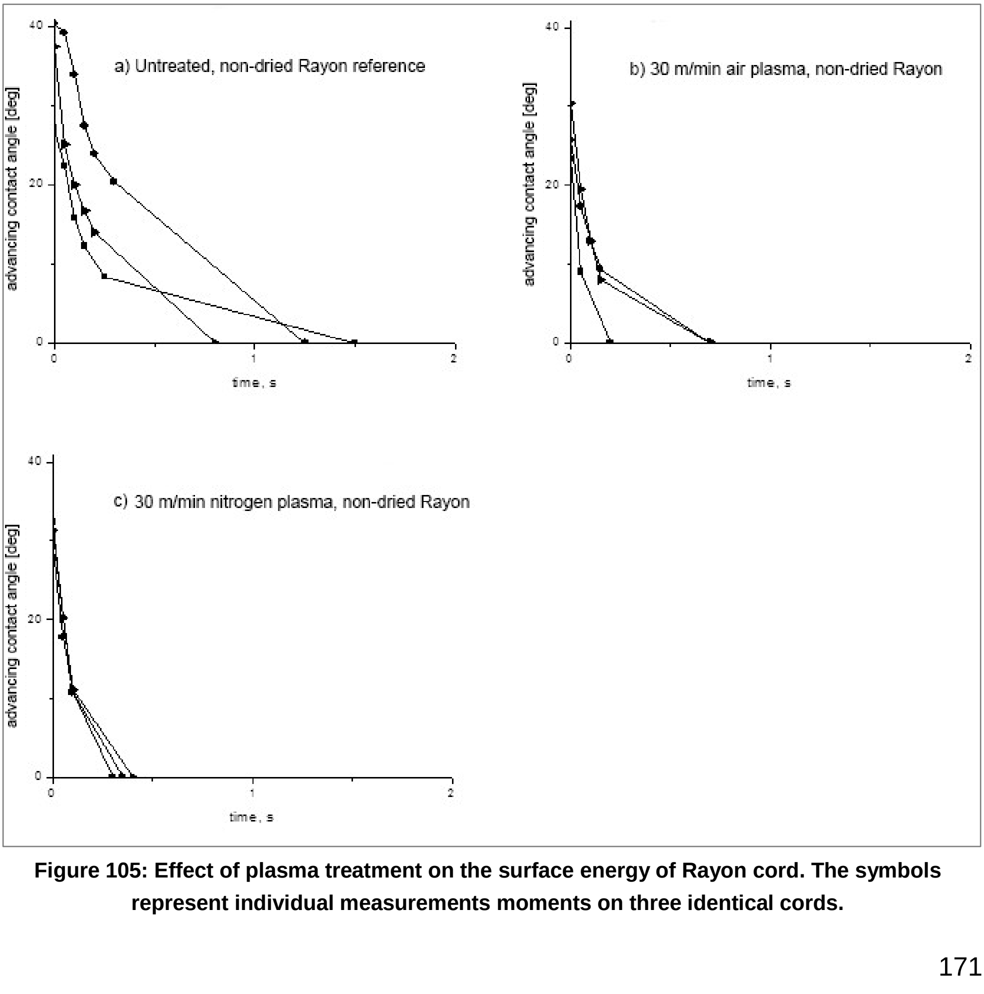


Figure 105: Effect of plasma treatment on the surface energy of Rayon cord. The symbols represent individual measurements moments on three identical cords.

In contrast to Rayon, for PET the time scale to measure the advancing contact angle is much smaller: it is measured in milliseconds instead of seconds for Rayon. This indicates that PET is much more hydrophilic than Rayon. The effect of the plasma treatment is much less pronounced in the case of PET cord: Figure 106 a, b, c. Taking the variation between the measurements into account, no significant differences can be measured between the untreated and the two plasma treated samples.

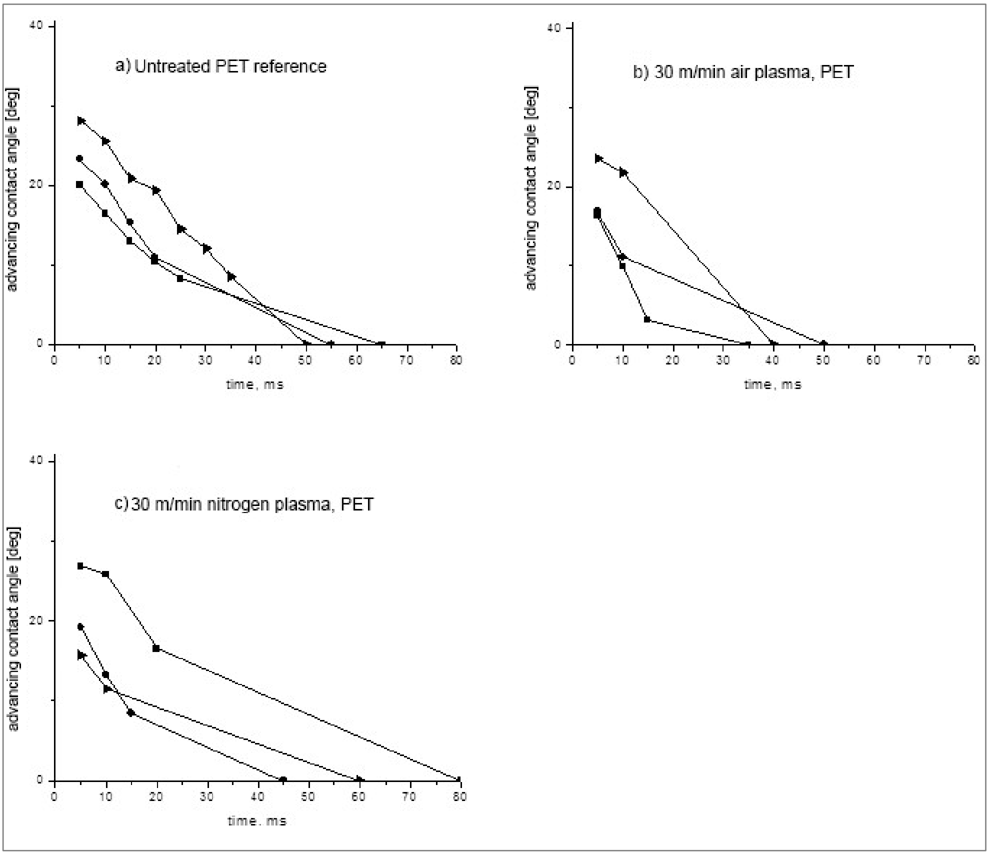


Figure 106: Effect of plasma treatment on the surface energy of PET cord. The symbols represent individual measurements moments on three identical cords.

Overall, the surface energy and thus the hydrophobicity and polarity of PET cord is clearly much less affected by plasma treatment, as neither the advancing contact angle nor the time factor do change like it was the case with Rayon cord. The behavior of PET without plasma treatment is already highly hydrophilic, which is why plasma treatment cannot further enhance that property. This result further underlines, that the PET surface is rather inert to plasma treatment, unlike Rayon cord which allows more possibilities to tailor its properties.

7.3 EFFECT OF THERMAL AGEING

The effect of ageing was analyzed after treatment in a hot air oven. The focus was on two different scenarios: (1) vulcanized H-pullout specimens of both cord types were exposed to elevated temperatures of 70°C for up to two weeks. With those specimens, the cord is fully covered with rubber and the samples were stored loose in the hot air oven. (2) Rayon cord, which was rubberized but not yet vulcanized, was first aged, then embedded into the test compound and finally cured. Then tensile and H-pullout tests were performed. Unaged reference samples have been measured for both test setups.

7.3.1 Ageing of vulcanized samples

Rayon cord – Four different Rayon samples were used in this thermal ageing test. For reference purposes, an untreated cord sample and the mandatory RFL sample were tested. Additionally, two identical thiophene plasma treated samples were aged as well, where one of them was rubberized right after the plasma treatment under a protective nitrogen atmosphere. From each Rayon cord type, 30 H-pullout samples were produced. Five of them (called REF) were tested after allowing them to relax at ambient temperatures for 24 hours. The remaining samples were put, after allowing them the same relaxation time, into the hot air oven which was set at a constant temperature of 70°C. After one, three, five, seven and fourteen days, another batch of five samples was tested for each of the four Rayon types. All samples got 15 minutes to cool down time before being tested. The results are shown in Figure 107. All samples basically follow the same trend. The highest H-pullout force was achieved with the unaged samples. Being exposed to 70°C caused an initial drop in adhesion, so that all samples lost in performance already within the first 24 hours. The RFL variant suffered the most, but it started from the highest overall initial value. At the other end of the scale, the untreated virgin sample had the smallest drop, but also the smallest initial adhesion forces.

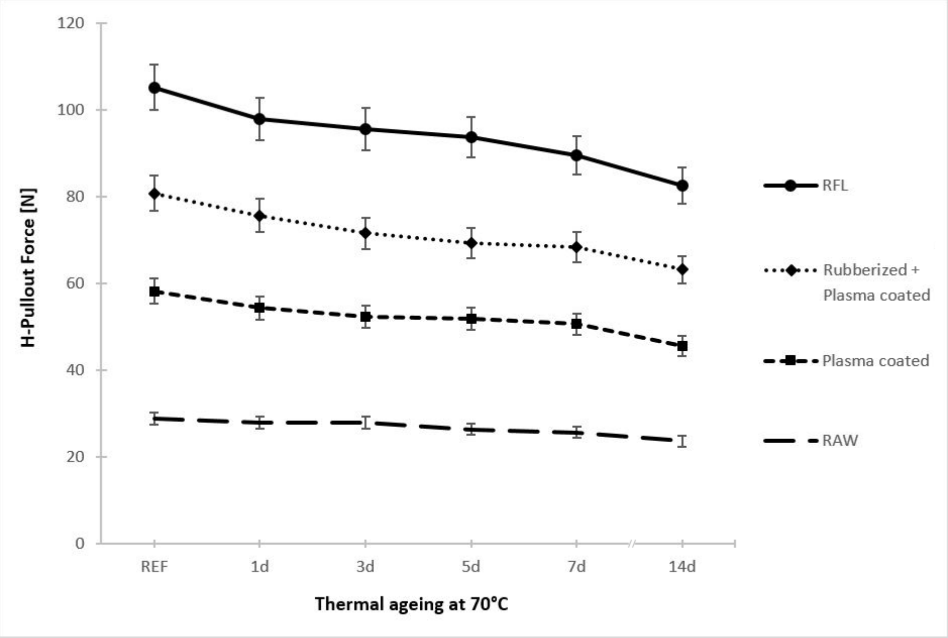


Figure 107: Thermal ageing of Rayon cord samples on H-pullout force.

After an initial strong decrease, the RFL cord stabilized again and the performance loss slowed down for the next 96 hours until reaching five days of ageing. In this last period, the H-pullout forces were still reduced, but at a slower pace. The plasma treated and rubberized Rayon cord had a consistent loss in performance for the first five days of ageing. For the next 48h there was almost no loss of performance anymore. The plasma treated, but not rubberized Rayon cord lost its properties on a lower level; between one and seven days of ageing the loss was less significant than it was for the other treated cords. However, it also had the lowest starting value of these three treated samples.

In Figure 108, a comparison of the measured loss of performance for 14 days is made. Clearly, the untreated virgin cord has the lowest loss of adhesion for the previously explained reasons, in absolute values as well as percentage of the initial value. However, the difference between the samples is less pronounced when expressed in percentages: the higher the initial adhesion force (see **Figure 107**), the higher the overall drop. The plasma coated and non-rubberized Rayon cord benefits from relatively small losses between day one and seven, otherwise it would have come very close to its rubberized counterpart. Generally spoken, all treatment types suffer in an comparable way from the hot air ageing, as the performance loss relative to their start values is for all three treated samples within 0,6 %, while the untreated reference losses about 5 % less.

A point of discussion is, that the ageing conditions for the rubberized samples are also harsh for the rubber itself. The question is, whether oxidative ageing penetrates in-between the cord and the rubber surrounding in the H-pullout test? In fact, all three relative decreases in adhesion strength in Figure 9 are practically the same (with exception of the virgin non-adhering reference sample). This is a difficult point to answer based on the present experiments.

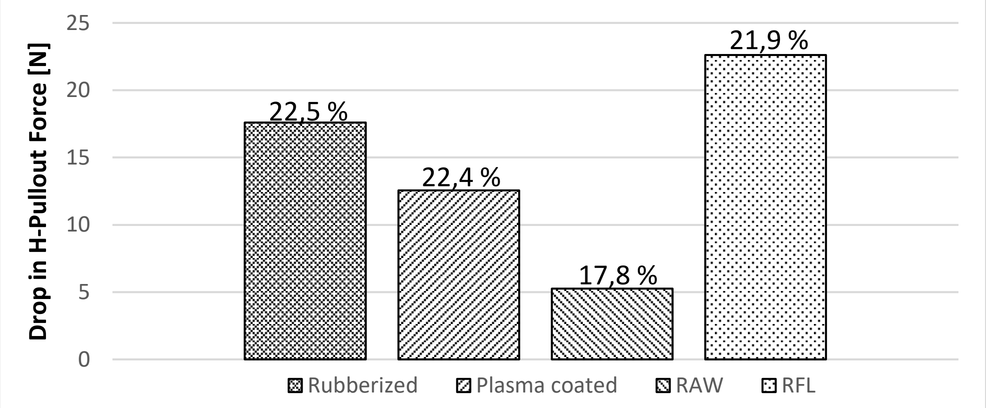


Figure 108: Comparison of performance loss of Rayon cord after 14d of ageing. Percentage values represent the relative performance loss.

PET cord – Unlike with the previously described Rayon cord, the polyester cord was not plasma treated with a thiophene coating, but treated with an H_2O plasma treatment. The interaction with the rubber was then established with bis[3-(triethoxysilyl)propyl] tetrasulfide (TESPT), which was incorporated into the rubber compound. For details about the treatment and processing see Chapter 5. Due to this special treatment process, no rubberized samples are available.

The highest H-pullout forces are reached with the RFL coating. The H_2O plasma treated sample has roughly two-thirds of the adhesion force of the RFL-treated sample, and the untreated virgin sample about one-third. The RFL sample loses less of its initial performance within the first 24 hours of ageing compared to the plasma treated sample, but the loss is then more pronounced in the next 48 hours. It stabilizes for the next 4 days, before it has another clear drop between 7 and 14 days of ageing. The loss of performance in the second week of ageing is more pronounced than for the plasma treated sample. The latter shows a significant loss of adhesion within the first 24 hours, but then continues with a slow and consistent reduction of H-pullout force till the end of the test. Comparing both treatment versions directly, one can say that the loss of adhesion is overall on the same level. But while the plasma treated sample loses most of its strength within the first 24 hours, the RFL sample suffers less at the beginning and has a stronger drop during the ongoing ageing. The untreated virgin polyester sample has clearly the least interaction with the rubber and therefore the lowest adhesion forces from the start. While it loses also performance, the loss is insignificant compared to the other samples. Again, the overall lack of adhesion prevents that the ageing can have a more significant effect here.

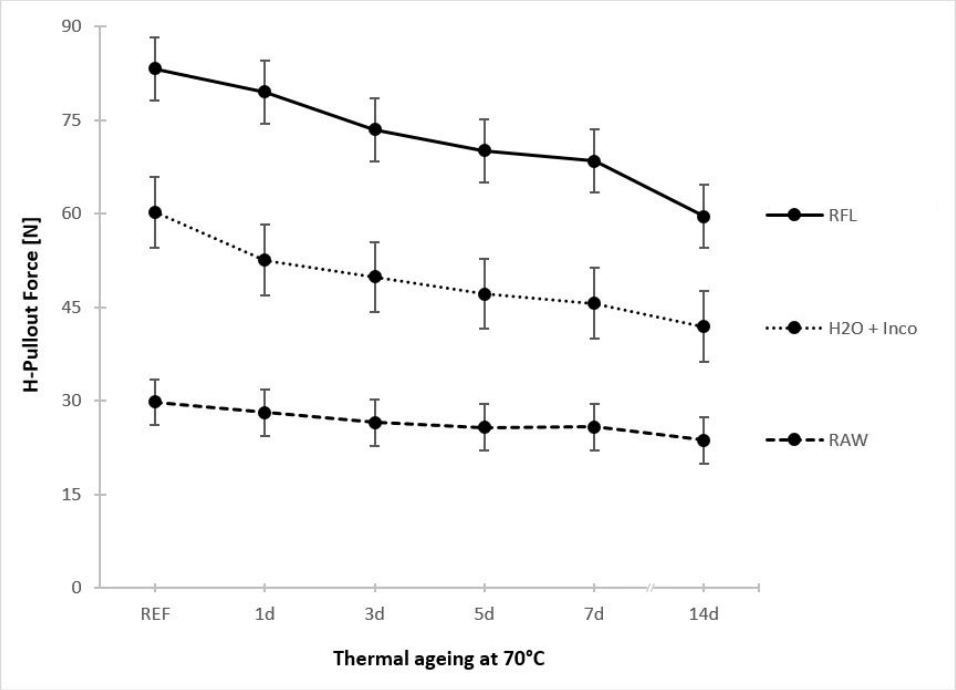


Figure 109: Thermal ageing of polyester cord samples.

Figure 110 shows the loss of adhesion within fourteen days of ageing at 70°C in a hot air oven. While RFL has the highest overall adhesion, it also decreases the most with the given test time. Also, the plasma treated sample has a strong decrease in H-pullout force, a bit less compared to RFL, but clearly more than the untreated virgin sample. However, the effect was expected and is like what was seen with Rayon before.

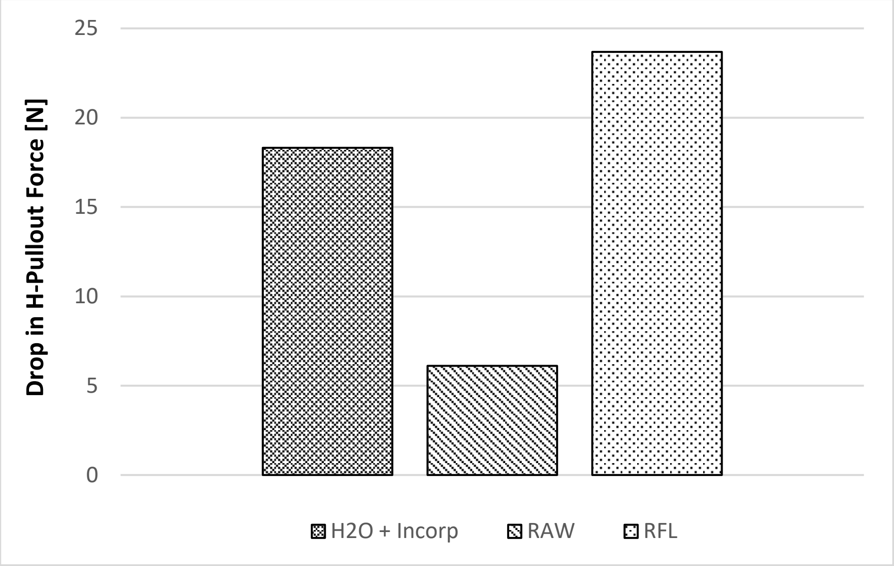


Figure 110: Comparison of performance loss of PET cord after 14 days of ageing.

Looking overall at all samples from Rayon and PET, it can be concluded, that there is a loss of adhesion due to thermal ageing at 70°C independent from the adhesion promotion type. The strongest ageing effect can be found for the RFL samples, followed by the plasma treated samples. As the RFL system gives the strongest adhesion forces, it is to be expected that the loss due to ageing is most significant here. Besides, the composition of the RFL-coating, especially the rubber component, are prone to ageing. The plasma treatment is more stable under these circumstances. This could be seen with both type of cords. However, independent of the plasma treatment type, both cords showed strong performance drops as well with this type of adhesion promotion. The performance drop is the lowest, when the overall adhesion is low from the start, which was the case for the untreated virgin cords. In both cases the drop was negligible and almost within the measurement error. While the adhesion promotion systems have clearly different ways of how they provide the adhesion between rubber and cord, they all are vulnerable to thermal ageing.

7.3.2 Ageing of cord material before vulcanization

As it became obvious, that all samples - independent of the adhesion promotion method - in the vulcanized state are decreasing in adhesion force overtime at elevated temperatures in a similar way, the question raised how ageing of the cord material itself would affect its performance. This then also generates an answer to the earlier raised question in the present chapter, whether ageing of the rubber in the H-pullout test is affecting the results.

To study this in more detail, the pure reinforcing cords were put as well into a hot air oven at 70°C. The frequency of taking samples was again one, three, five, seven and fourteen days. The cord materials were then used to prepare H-pullout samples which were vulcanized and then allowed to rest for 24 hours prior to testing.

Rayon cord – For the RFL sample there was a significant drop noticeable after 24 hours of ageing. Beyond that point, the effect of thermal ageing was still detectable, but the performance drop is not significant anymore. The trend remains constant until the end of the test. The thiophene plasma treated and rubberized sample aged differently. There is no sudden drop in performance, but a steady and consistent loss over the whole testing time: the rubber coating protects the cord surface also at elevated temperatures which prevents a huge drop of adhesion force. This clearly becomes a fact, when the non-rubberized sample is considered too. It had a significant drop in performance within the first 24 hours, but decreases further during the test and dropped again in the second week of ageing. Overall, its performance dropped almost to the one of the untreated virgin cord and therefore, lost all its initial benefits received from the plasma coating. The thermal ageing does not affect the adhesion properties of the untreated virgin cord, however low the adhesion.

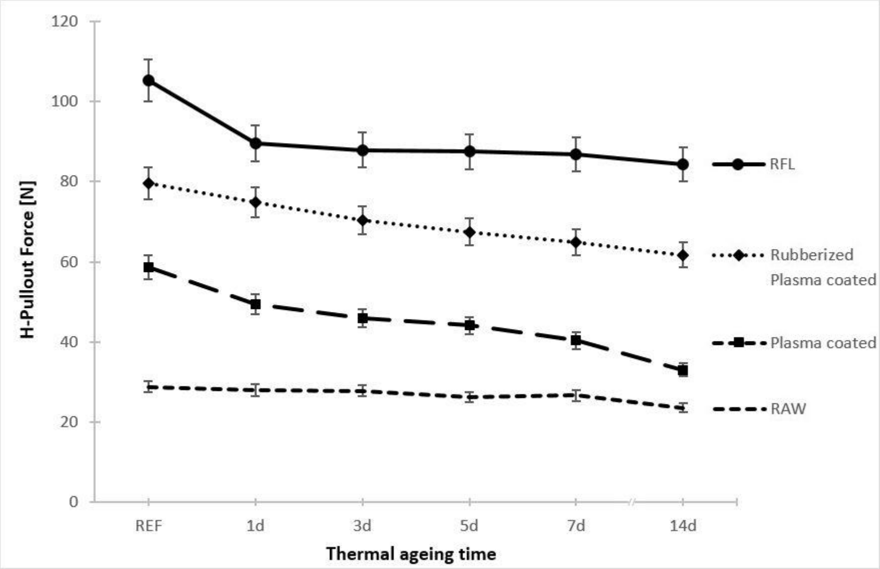


Figure 111: Thermal ageing of Rayon cord material, where the cord samples were aged prior to vulcanization.

Unlike the performance losses seen previously in Figure 108, the constellation now changed due to the reinforcing cord ageing, as is shown in Figure 112 below. Clearly, the plasma treated non-rubberized Rayon cord had the highest loss in performance with about 26 N over the whole ageing period. The RFL cord follows with a loss of ca. 23 N, and then the plasma treated rubberized cord comes with 18 N of performance loss. Identical to the previous situation, the untreated cord does not suffer much from the thermal ageing, as it does not deliver a reinforcing effect at any time.

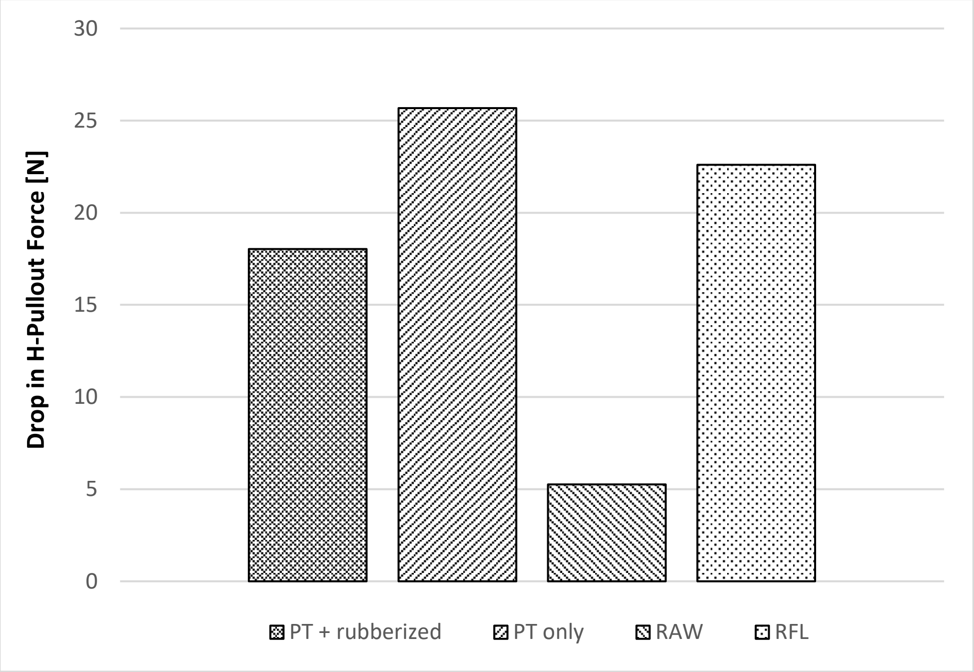


Figure 112: Comparison of performance loss of Rayon cord after 14 days of ageing.

Besides the adhesion force, measured in H-pullout tests, also the tensile strength of the aged reinforcing cords was analyzed. The tensile test was performed according to ASTM 887 (see Chapter 3) and with the same cord material as used for the H-pullout samples. The question was, if the reinforcing cord itself suffers a performance loss too. The results are shown in Figure 113. The rubberized cord was not tested in this case, as the rubber coating was not removable and a proper fitting of such a cord in the tensile tester was not possible.

It is obvious that the thermal ageing had no effect on the cords, as they all keep a consistent performance over the whole ageing period. The untreated cord reaches the highest forces at break, followed closely by the plasma treated cord.

The RFL type cord as such has an about 30 N decreased force at break, together with a reduction of the elongation at break, which indicates a stiffening effect of the RFL coating procedure on the Rayon cord. This is in line with the measurement results seen in Figure 100 of this chapter. From this measurement can be concluded, that the coating of the cords does decrease the adhesion force over time, while the reinforcing cords themselves do not loose performance under these thermal ageing conditions of fourteen days at 70°C. This is a problem for the unprotected plasma treated Rayon cord, which lost almost all of its adhesion promotion properties during this ageing test.

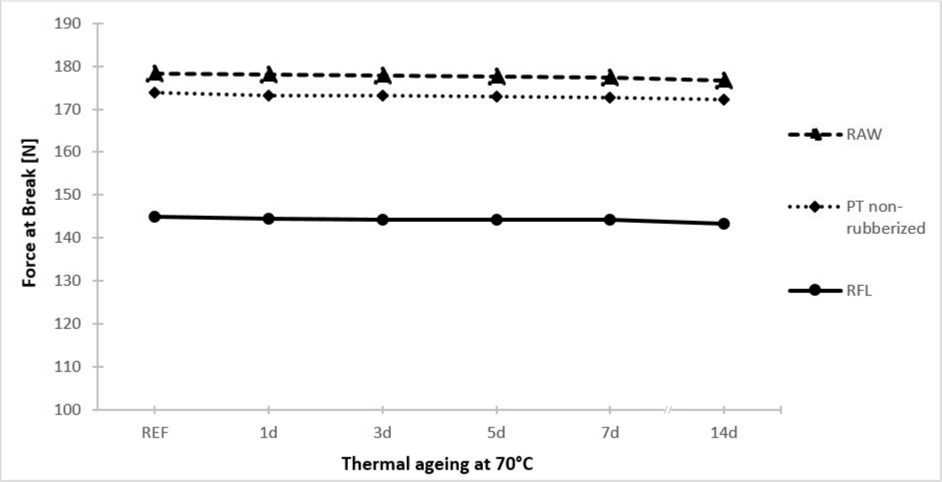


Figure 113: Force at Break of Rayon cord, measured in a cord tensile test, development over 14 days of ageing.

PET cord – Three polyester cords were compared with each other. One cord was plasma treated with H_2O as precursor in a nitrogen plasma under atmospheric conditions and treated with TESPT, one cord was not treated at all, and the third one was the RFL coated variant.

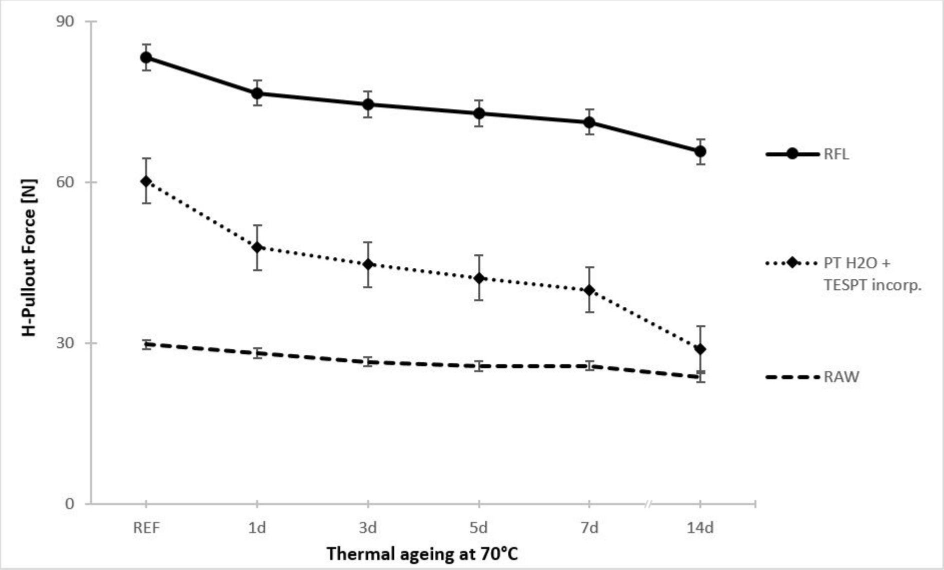


Figure 114: Thermal ageing of PET cord material, where the cord samples were aged prior to vulcanization.

In Figure 114, the H-pullout force is plotted over the duration of ageing at 70°C. The plasma treated sample is severely damaged in performance due to the ageing. Within the first 24 hours there is a significant drop in adhesion force. Over the next 144 hours there is another continuous loss of adhesion, but to a lesser extent. Within the second week of ageing, the effect of the plasma treatment almost entirely vanished. The cord performance comes very close to the one of the untreated sample at the end of the test. The RFL coated sample performs significantly better. It also has a drop of performance within the first 24 hours of ageing, but the trend is stopped and only a small loss in performance is noticeable during the next time intervals. The overall ageing behavior is like the Rayon-RFL cord: see Figure 111, but for PET the initial drop is less, and the ageing is more pronounced with ongoing time than with its Rayon equivalent. The untreated polyester cord is again not significantly affected by the thermal ageing. This can also be seen in Figure 115, where the bars represent the overall loss in H-pullout force during the entire thermal ageing time. Clearly, the plasma treated sample is affected the most. Apparently, the hydroxide moieties introduced to the cord surface during the plasma treatment undergo a condensation reaction, which leads to this reduction of adhesion strength at elevated temperatures of the thermal ageing process. The concentration of OH-groups on the surface is decreasing, meaning that TESPT has increasingly less reaction possibilities with ongoing ageing time. Therefore, the unprotected H_2O plasma treated cord is very sensitive to ageing and elevated temperatures, and it is recommended to process the cord as soon as possible after the plasma treatment to gain the maximum effect. This is certainly a disadvantage of plasma treatment in comparison with RFL.

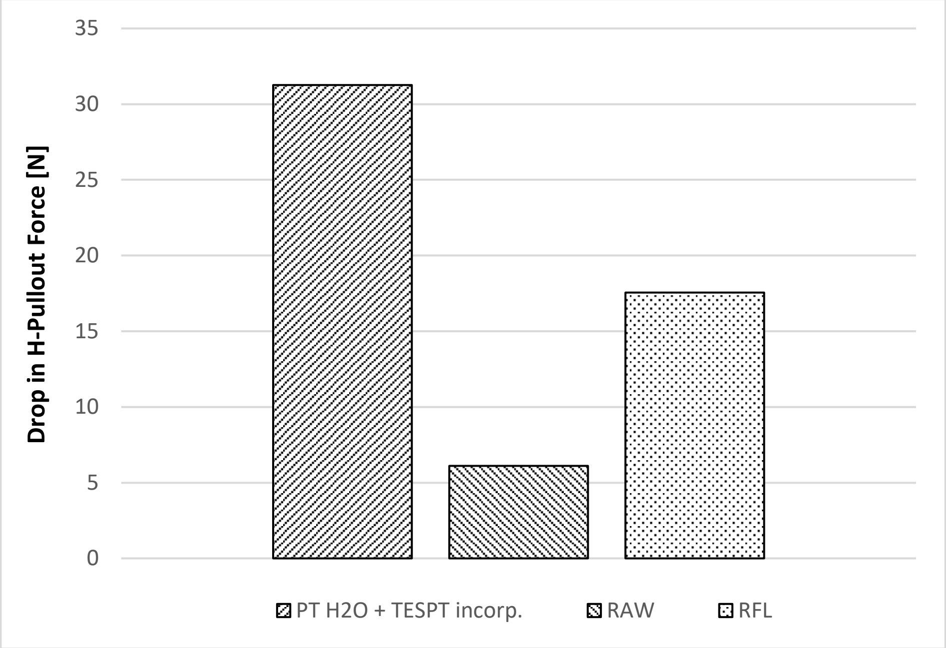


Figure 115: Comparison of performance loss of PET cord after 14 days of ageing.

7.4 CONCLUSIONS

In this chapter, it was shown that the mechanical properties of the cord, before and after it was rubberized, depend to a certain degree on the processing conditions. Changes of these properties like they occur during the application of an RFL dip, can be achieved with plasma treatment as well. For Rayon, a nitrogen plasma treatment with a cord winding speed between 7.5 and 15 m/min was suitable to shift the cord properties close to the one of a RFL dipped cord. In case of PET, an air plasma with a cord winding speed of 30 m/min was the best choice. Tailoring of these properties is possible with plasma treatment. The heat that the cord is exposed to during either treatment is a principal factor, as it has an influence on the RFL dipped as well as on the plasma coated cord, and therefore defines the cord properties used for the tire construction.

The surface energy is affected by plasma treatment. The effect is more noticeable for Rayon cords than for the polyester cords. The effect appears to be permanent, as it remains present even weeks after the actual plasma treatment. Therefore, it is a good technique to tailor the hydrophilic character of Rayon. The PET surface proved that it is indeed inert, as it was not affected by the plasma treatment.

The thermal stability of the cords is also an important factor for the plasma treatment process: PET is highly sensitive to the heat exposure by the plasma source. A slow winding speed, effectively below 30 m/min, caused severe defects on the cord surface and a strong loss in mechanical properties.

The thermal ageing of vulcanized H-pullout samples in a hot air oven at 70°C showed, that all adhesion promotion systems are sensitive to this. There is no significant advantage of one system over the others. While RFL showed the best initial adhesion force, it suffered the most as the performance loss during ageing significant. This is true for both cord types, polyester and Rayon. Overall, the effect of thermal ageing on adhesion force was independent from the adhesion system, because a higher initial adhesion value resulted in a higher decrease in performance over time.

The reinforcing cord itself was – prior vulcanization of the test specimens – also exposed to thermal ageing. Interestingly, the RFL still exhibited the best performance, while the ageing was found to be most prominent during the first 24 hours. It stabilized afterwards and did not show further drops in performance, as noticed for Rayon and PET. The behavior of the plasma treated samples is different. While the thiophene coated and rubberized Rayon cord showed a relatively slow but steady loss of performance, the unprotected or non-rubberized plasma samples performed poorly after ageing. They suffered from an early drop of performance, which continued further with the ongoing residence time in the hot air oven. The H_2O plasma treated polyester sample degraded so heavily, that it lost all the beneficial effects from its treatment. Therefore, it is crucial that the plasma treatment is immediately followed by further processing steps to protect the effect of plasma treatment. Once a protective layer is in place, the cord can be stored and further processed prior to vulcanization. The reinforcing cord itself is not affected much by thermal ageing: tensile tests showed very stable results in mechanical properties over the whole ageing period. This indicates, that the cords can accept elevated temperatures, but the adhesion promotion system applied to the cord surface does loose a significant amount of its ability to adhere to rubber over time.

SUMMARY

The aim of the present thesis is, to apply plasma treatment on polymeric reinforcing single end cords to promote adhesion between these cords and rubber. In general, polymeric reinforcing cords do not adhere well to rubber compounds without further treatment. The lack of adhesion is caused by a polar and inert cord surface, which is very smooth too. Furthermore, those cords are featuring a high modulus that causes a high stiffness, that further reduces the compatibility to rubber. To reach an appropriate level of adhesion it is necessary to apply an adhesion promoting treatment. Reinforcing cords usually undergo a dip process where a Resorcinol-Formaldehyde-Latex (RFL) coating is applied, which migrates into the upper layers of the cords and is cured with a heat treatment. Depending on the cord type, an initial epoxy coating is applied before the actual RFL-treatment. The main reason to do research on plasma treatment as an alternative is the risk, that the legislation may act against key ingredients of the RFL-dip due to their toxicity.

Plasma treatment is a promising candidate, because of its ability to perform surface treatments which chemically alter the surface properties. Furthermore, plasma technique is nowadays small and compact as well as applicable under atmospheric conditions. This makes it highly interesting for industrial applications. The plasma line used in the present thesis was developed from a basic setup with a winding unit and a single plasma device to a sophisticated treatment line which utilizes several processes with dedicated and specialized solutions.

The plasma treatment part of the line in its final development status consists of two pairs of atmospheric pressure plasma jets (APPJ). The first APPJ pair is used for the application of a strong plasma, where an etching effect causes the decontamination of the cord surface. The second APPJ applies a plasma polymerization process, which is responsible for the deposition of chemicals on the cord surface. This processing step adds new functional groups to the cord surface, that can be used for crosslinking with rubber during vulcanization. Therefore, this

APPJ pair is equipped with a precise pump, which delivers the chemicals, called precursors, that are injected into the plasma stream.

Around these plasma jets a treatment chamber was created within the present work. The tailored layout consisted of a steel chamber, that must withstand excessive heat from the plasma jets under operating conditions. The sealing of the chamber and the application of a slight overpressure with a protective gas helped to avoid that oxygen can enter the chamber. The main advantage of the final design of the plasma treatment chamber was the removal of exhaust gases, as they caused problems in adhesion performance in first instance. Besides the treatment chamber itself, a constant protective environment during and after the plasma treatment till the cord is rubberized is crucial. The peripheral equipment developed for the plasma line includes a section for pre-treating the cord, a tension control system, a precursor supply unit, an exhaust extraction system, a dipping bath, a crosshead-extruder and a winding unit.

Scaling-up of this line from its current pilot scale to a full sized industrial process will require a significant amount of effort. The current treatment speed of about 10 m/min for a single end cord is too low, when the amount of cord required per tire is about 1,5 km. Currently, the control of the layer thickness of the deposited precursor is highly dependent on the cord speed. When the cord speed is increased to a level that is required for an industrial treatment process, a plasma equipment becomes necessary that can control the layer thickness independently. Besides, the efficiency of the current setup is rather low. However, this pilot scale plasma line was built to prove the concept of using plasma treatment for adhesion promotion between rubber and polymeric cords, and that was indeed successful.

A major topic in the present thesis are sulfuric precursors. The aim is to plasma polymerize these precursors to form a polymeric layer on the cords surface, and also to crosslink this layer with the cord surface to form a strong bond due to the active radicals of the plasma. This layer should adhere due to its covalent bondage to the cord and at the same time enhance adhesion towards rubber. The plasma polymerized layer reduces the polar nature of the cord, and its sulfuric groups can interact with the rubber during vulcanization. Several mono- and polysulfidic precursors are tested and validated.

A strong increase of adhesion between rayon and rubber is achieved with thiophene as precursor. The enhancement is measured by two mechanical tests methods: the H-pullout test and SPAF test. The improvement with this precursor is significant, as it nearly reaches the desired level of a RFL-coated cord. However, the failure mode is clearly different. In case of a RFL treatment the failure that occurs is cohesive, thus mainly in the rubber phase, this is not the case for the plasma treated cords. In the latter case, the outer filaments of the cords fail first when a load is applied. The remaining filaments in the rubber phase are evidence for chemical adhesion. Therefore, the achieved results with Rayon cord are satisfying and the desired adhesion level is nearly reached with the developed plasma line.

Several attempts were done to analyze the polymerized layer in detail. In literature, mainly FT-IR and XPS techniques are used for that purpose. This analysis would help to understand, why certain precursors are not able to promote adhesion. However, in the present work those techniques were unable to identify differences between the untreated cord and its plasma treated counterpart, while mechanically the effect of the plasma treatment is clearly measurable.

The requirements for the plasma precursor for adhesion promotion with Rayon cord are well understood in the present thesis. Experiments with different sulfuric precursors clearly show, that only thiophene can significantly improve the cord-rubber adhesion. Its unique property compared to the other precursors is the ring-structure in its molecular configuration. The structure of thiophene allows the best reactivity when exposed to the plasma. It is assumed that other sulfuric precursors get entirely atomized in the plasma and recombine in a rather chaotic manner. The created plasma polymerized layer on the cord surface has no repeating elements and only a very limited number of functional groups, that can react with the rubber during vulcanization. Therefore, their ability to adhere to an elastomeric matrix is low. Thiophene can plasma polymerize with a more stable molecule that is easier to activate. Consequently, the created polymeric layer has much more repeating units with a significantly higher number of functional groups, resulting in the ability to create a significantly higher level of adhesion. A comparison of thiophene with pyrrole, that has a similar molecule structure, but in which the sulfur atom of the thiophene is substituted by a secondary amine, indicates the importance of a sulfur atom in the ring structure. While thiophene performs well, pyrrole can enhance the adhesion level only slightly. Clearly, the sulfur atom of thiophene helps with the interaction of the plasma polymerized layer with the formed sulfur complexes during vulcanization. Another comparison of thiophene with tetrahydrothiophene further underlines the importance of double bonds in the ring structure, which are entirely absent in case of tetrahydrothiophene. This causes a less stable ring which probably gets cracked during the exposure to the plasma and prevents a similar plasma polymerization like achieved with thiophene.

Besides those requirements for the precursor molecule, it is understood that a plasma treatment with nitrogen prior to the precursor applications is necessary to achieve good adhesion results. It is shown, that it is not only important to use nitrogen as ionization and precursor gas, but also to create a protective atmosphere around the cord until it is rubberized. The much higher reactivity of oxygen when using air as ionization gas deactivates the freshly plasma treated cord and therefore, prevents a successful bonding of the plasma polymerized layer with the rubber. Further, the plasma power setting of the generator and the precursor flow rate have a strong influence on the adhesion values.

The treatment of polyester (PET) cord with sulfuric precursors does not show the same positive effect, even when the process optimizations achieved with Rayon are applied. Clearly, polyester is a very heat sensitive material that does not allow aggressive plasma settings, which would have been necessary to overcome the materials inertness. As the sulfuric precursor plasma treatment are not applicable for polyester, another inventive plasma solution is required for polyester.

This alternative inventive solution turned out to be the application of coupling agents known from silica compounds in combination with a plasma treatment that creates hydroxyl groups on the cord surface. TEOS was chosen precursor as initial precursor. It was found that TEOS is unable to form the required functional groups to react with the coupling agents in the plasma. But with demineralized water, which has many advantages like no toxicity, ease of handling, no environmental burden, etc., a novel route was developed. This technology unveils the best PET adhesion values reached with plasma treatment, and the DoE test series shows which parameters are relevant for a high adhesion level. However, the RFL cords still show overall the highest adhesion values.

A disadvantage of this technique is, that it requires further processing after the plasma treatment to incorporate a coupling agent. Unfortunately, the coupling agents in a silica compound reacted already when the cord-rubber bond is made; they cannot react furthermore with the cord surface. Therefore, a separate cord silanisation step is mandatory.

The penetration depth of rubber into the cord structure is a crucial parameter for good adhesion. However, the general statement that a penetration depth of 4 filament-layers is ideal could not be confirmed, as it did not give the expected highest adhesion level. The pressure exerted in the extruder head when rubberizing the cord after the plasma treatment was expected to have a considerable influence on the penetration depth. In actual practice there is no direct correlation between extruder pressure, penetration depth and adhesion: the highest pressure did not lead to best penetration nor adhesion. Explanations for this effect might be, that a high pressure in the crosshead compresses the cord too much which prevents a deeper penetration. With optimized extruder settings, a greater number of filaments is attached to the rubber, but the adhesion results stagnate on a certain level. This is taken as an indication, that the plasma coating does not reach deeper filament layers and is indeed a pure surface treatment. A failure mechanism which points into a similar direction with respect to plasma penetration depth and adhesion strength was observed: the outer filaments embedded in rubber do separate from inner sections of the cord. This means, that the adhesion between these filaments and the rubber is stronger than their connection to the core of the cord.

The mechanical properties of the cord depend to a certain degree on the processing conditions when applying an adhesion promotion. Changes of these properties like they occur during the application process of an RFL dip, can be achieved with plasma treatment as well. For Rayon, a nitrogen plasma treatment is suitable to shift the cord properties close to the one of a RFL dipped cord. In case of PET, an air plasma is the best choice to affect the mechanical properties. Tailoring of these properties is possible with a plasma treatment. This is a key factor, as this side effect of the adhesion promotion treatment has a significant effect on the RFL dipped as well as on the plasma coated cord and determines the properties used for the tire construction. The surface energy is affected by plasma treatment too. The effect is more noticeable for Rayon cords than for the polyester cords. The effect appears to be permanent, as it remains present even weeks after the actual plasma treatment. Therefore, it is a good technique to tailor the hydrophilic character of Rayon. The PET surface proved that it is indeed highly inert, as it was not affected by the plasma treatment in terms of surface energy. The thermal stability of the cords can become an issue in the plasma treatment process: PET is sensitive to the exposure of heat by a plasma source. Slow winding speeds can cause severe defects on the cord surface and a strong loss in mechanical properties.

Thermal ageing of vulcanized H-pullout samples in a hot air oven at 70°C showed, that all adhesion promotion systems are sensitive to this type of ageing. There is no significant advantage of one system over the others. While RFL shows the best initial adhesion force, it has the highest loss in performance during ageing. This is true for both cord types, Rayon and PET. Overall, the effect of thermal ageing on the adhesion force is independent from the adhesive system.

The reinforcing cord itself was – prior to vulcanization of the test specimens – also exposed to thermal ageing. Interestingly, the RFL still exhibited the best performance, with ageing being most prominent during the first 24 hours. It stabilized afterwards and did not show further drops in performance, which is valid for Rayon and PET. The behavior of the plasma treated samples is different. While the thiophene coated and rubberized Rayon cord showed a relatively slow but steady loss of performance, the unprotected or non-rubberized plasma samples performed poorly under these ageing conditions. They suffer from an early drop of performance, which continues with increasing residence time in the hot air oven. The H_2O plasma treated polyester sample degrades so heavily, that it losses all the beneficial effects from its treatment. Therefore, it is crucial that the plasma treatment is immediately followed by further processing steps to protect the effect of plasma treatment. Once a protective layer is in place, the cord can be stored until further processing prior to vulcanization. The reinforcing cord itself is not affected by thermal ageing: Tensile tests showed very stable results in mechanical properties over the whole testing period. This indicates, that the polymeric cords can accept elevated temperatures, but the adhesion promotion system applied to the cord surface does loose a significant amount of its ability to adhere to rubber over time.

SAMENVATTING

Het doel van het onderhavige proefschrift is het toepassen van plasma-behandeling op polymere versterkende enkelvoudige koorden om hechting te bevorderen tussen zulke koorden en rubber. In z'n algemeenheid hechten polymere versterkende koorden niet goed aan rubber mengsels zonder verdere behandeling. Het gebrek aan hechting wordt veroorzaakt door een polair en inert koord-oppervlak, welk zeer glad is. Bovendien hebben zulke koorden een hoge modulus, wat een hoge stijfheid ten gevolge heeft, hetgeen de verdraagzaamheid met rubber verder verlaagt. Om een voldoende adhesie-niveau te verkrijgen moet een hechting-bevorderende behandeling worden toegepast. Versterkende koorden worden gewoonlijk onderworpen aan de zgn. "dip"-proces, waarin een Resorcinol Formaldehyde Latex (RFL)-hechtlaag wordt aangebracht, die in de bovenste lagen van de koorden migreert en wordt uitgehard met een warmtebehandeling. Afhankelijk van het type koord wordt voorafgaand aan de RFL-behandeling een epoxy-laag aangebracht. De hoofdreden om onderzoek te doen naar plasma-behandeling als alternatief is het risico, dat toekomstige wetgeving zich gaat keren tegen de belangrijkste ingrediënten van de RFL-dip vanwege hun giftigheid.

Plasma-behandeling is een veelbelovende kandidaat vanwege het vermogen om oppervlaktebehandelingen uit te voeren, die de chemische oppervlakte-eigenschappen veranderen. Bovendien is plasmabehandeling tegenwoordig kleinschalig en compact en toepasbaar onder atmosferische omstandigheden. Dit maakt het hoogst interessant voor industriële toepassingen. De plasma-lijn gebruikt in het onderhavige proefschrift is ontwikkeld vanuit een simpele begin-opstelling met slechts een opwind-eenheid en een enkelvoudig plasma-apparaat, in een geavanceerde versterkende koord-behandelingslijn, die verschillende processen omvat met gerichte een gespecialiseerd oplossingen.

Het plasma-behandelings-deel van de finale ontwikkelingsstatus van de lijn bestaat uit twee paren plasmajets voor atmosferische druk (APPJ). Het eerste APPJ-paar wordt gebruikt voor de toepassing van een sterk plasma, waardoor een etsend effect een ontsmetting van het koord-oppervlak bewerkt. Het tweede APPJ-paar met plasma polymerisatie-mogelijkheden is verantwoordelijk voor de depositie van chemicaliën op het koord-oppervlak. Deze proces-stap voegt nieuwe functionele groepen toe aan het koord-oppervlak, die kunnen worden gebruikt voor de vernetting met rubber gedurende vulkanisatie. Daarvoor is dit paar voorzien van een precisie-pomp, die de chemicaliën aanlevert, die precursors worden genoemd, en worden geïnjecteerd in de plasma stroom.

Rond deze plasma-jets is een behandel-kamer geconstrueerd in het huidige onderzoek. Het ontwerp bestond uit een stalen kamer, daar het bestand moest zijn tegen extreme hitte van de plasma-jets gedurende gebruik. De afdichting van de kamer en de toepassing van een lichte overdruk met een beschermend gas hielp te voorkomen, dat zuurstof kan binnendringen in de kamer. Het belangrijkste voordeel van het finale ontwerp van de plasma behandelings-kamer was de verwijdering van af-gassen, daar zij in het begin problemen veroorzaakten in hechtings-gedrag. Naast de behandelkamer zelf is een constante beschermende omgeving gedurende en na afloop van de plasma-behandeling tot het koord wordt berubberd cruciaal. De hulp-apparatuur ontwikkeld voor de plasma-lijn omvat een sectie voor voorbehandeling van het koord, een trek-spannings-controle systeem, een precursor eenheid, een afgas-ontluchtingssysteem, een dip-bad, een kruiskop-extruder en een opwind-eenheid.

Opschalen van de deze lijn vanuit de huidige pilot-schaal naar een grootschalige industriëel proces zal e en significante hoeveelheid inspanning vereisen. De huidige behandel-snelheid van ongeveer 10 m/min. voor een enkelvoudig koord is te laag voor een hoeveelheid koord van 1,5 km nodig voor een autoband. Controle van de laagdikte van de opgebrachte precursor is in hoge mate afhankelijk van de koordsnelheid. Voor verhogen van de koordsnelheid tot een niveau vereist voor een industrieel behandelingsproces is plasma-apparatuur nodig, die de laagdikte onafhankelijk kan controleren. Daarnaast is de efficiëntie van de huidige opstelling nogal laag, Evenwel, deze pilot-schaal plasma-lijn was gebouwd om het concept te bewijzen van het gebruik van plasmabehandeling voor hechtingsbevordering tussen polymere koorden en rubber, en dat was inderdaad een succes.

Eén hoofdonderwerp in het huidige proefschrift zijn zwavelhoudende precursors. Het doel was om deze precursors met plasma te polymeriseren om een polymere oppervlaktelaag op de koorden aan te brengen, maar ook deze laag te vernetten met het koordoppervlak om zo een sterke binding te vormen vanwege actieve radicalen op het oppervlak. Deze laag moet hechten via covalente binding aan het koorden tegelijkertijd de hechting richting rubber bewerkstelligen. De plasma-gepolymeriseerde laag verlaagt of verhult de polaire aard van het koord, en z’n zwavel-groepen kunnen wisselwerken met de rubber gedurende vulkanisatie. Verschillende mono- en polysulfidische precursors worden getest en gevalideerd.

Een sterke hechtingstoename wordt bereikt tussen rayon en rubber met thiopheen als precursor. De verhoging wordt gemeten met twee mechanische test-methoden: de H-pull out test en de SPAF-test. De verbetering met deze precursor is significant, daar het bijna het gewenste niveau bereikt van een koord met RFL-coating. Echter de wijze van breuk is duidelijk verschillend. Terwijl in geval van een RFL-behandeling de breuk cohesief is, dus voornamelijk inde rubber-fase, is dat niet het geval voor plasma-behandelde koorden. In het laatste geval breken de buitenste filamenten van de koorden eerst wanneer een belasting wordt aangebracht. Het achterblijven van filamenten in de rubberfase is een aanwijzing voor chemische hechting. Daarom zijn de bereikte resultaten voor rayon koord voldoende en wordt het gewenste adhesie-niveau bijna bereikt met de ontwikkelde plasma-lijn.

Verschillende pogingen worden gedaan om de gepolymeriseerde laag in detail te analyseren. In de literatuur worden vooral de FTIR en XPS technieken gebezigd voor dat doel. Deze analyse kan helpen te begrijpen waarom bepaalde precursors niet in staat zijn om hechting te bevorderen. Echter, deze technieken waren niet in staat verschillen te detecteren tussen onbehandeld koord en z’n plasma-behandelde tegenhanger, ofschoon het effect van de plasmabehandeling mechanisch duidelijk meetbaar is.

De eisen te stellen aan de plasma precursor voor hechtingsbevordering aan rayon koord worden goed begrepen in het huidige proefschrift. Experimenten met verschillende zwavel-precursors laten duidelijk zien, dat alleen thiopheen de koord-rubber hechting significant kan verbeteren. Z’n unieke karakteristieke eigenschap in vergelijking met de andere precursors is de ring-structuur in de moleculaire configuratie. De thiopheen-structuur geeft de beste reactiviteit wanneer onderworpen aan plasma. Er wordt aangenomen, dat andere zwavel-precursors volledig worden ge-atomiseerd in de plasma en daarna recombineren op een nogal chaotische wijze. De gevormde plasma-gepolymeriseerde laag op het koord-oppervlak heeft daardoor geen repeterende elementen en slechts een zeer beperkt aantal functionele groepen, die kunnen reageren met de rubber gedurende vulkanisatie. Derhalve is hun vermogen om aan een elastomere matrix te hechten beperkt. Thiopheen kan plasma-polymeriseren met een stabieler molecuul, dat gemakkelijker te activeren is. Dientengevolge heeft de gecreëerde polymere laag veel meer repeterende eenheden met een significant verhoogd aantal functionele groepen, resulterend in het vermogen een duidelijk hoger hechtingsniveau te bereiken. Een vergelijking van thiopheen met pyrrool, wat een vergelijkbare moleculaire structuur heeft maar waarin het zwavel-atoom van het thiopheen is gesubstitueerd door een secundair amine in het geval van pyrrool, gaf het belang aan van een zwavel-atoom in de ring-structuur. Waar thiopheen goed voldoet, kan pyrrool het hechtingsniveau maar een klein beetje verhogen. Het zwavel-atoom in de thiopheen helpt bij de interactie van de plasma-gepolymeriseerde laag met de gevormde zwavel-complexen gedurende vulkanisatie. Een andere vergelijking van thiopheen met tetrahydrothiopheen onderstreept verder het belang van dubbele bindingen in de ring-structuur, die volledig ontbreken in geval van tetrahydrothiopheen. Dit veroorzaakt een minder stabiele ring, die waarschijnlijk breekt tijdens de plasma-behandeling en een vergelijkbare plasma-polymerisatie als met thiopheen verhindert.

Naast deze eisen aan het precursor molecuul wordt vastgesteld, dat een plasma-behandeling met stikstof voorafgaand aan het opbrengen van de precursor nodig is om goede hechtingsresultaten te bereiken. Er wordt aangetoond, dat het niet alleen belangrijk is om stikstof als ionisatie en precursor gas te gebruiken, maar ook om een beschermende atmosfeer rond de koord-eenheid creëren totdat deze wordt berubberd. De veel hogere reactiviteit van zuurstof bij gebruik van lucht als ioniserend gas deactiveert het verse plasma-behandelde koord en belemmert daardoor een succesvolle binding van de plasma-gepolymeriseerde laag met de rubber. Verder bleken de vermogensregeling van de plasma-generator en de stroomsnelheid van de precursor en sterke invloed te hebben op de hechtingswaard es.

Behandeling van polyester-koord met zwavel-precursors vertoont niet eenzelfde positief effect, zelfs niet wanneer de optimalisaties verkregen met rayon worden toegepast. Polyester is duidelijk een erg hitte-gevoelig materiaal, wat agressieve plasma-instellingen onmogelijk maakt, die nodig zouden zijn geweest om de inertheid van het materiaal te overwinnen. Daar de zwavelhoudende precursor plasma behandeling niet toepasbaar is voor polyester is een andere inventieve plasma-oplossing voor polyester vereist.

Deze alternatieve inventieve oplossing bleek de toepassing van coupling agents te zijn, bekend van silica-mengsels, in combinatie met een plasma-behandeling, die hydroxyl-groepen creëert op het koord-oppervlak. De aanvankelijk gekozen precursor bleek niet optimaal, daar Tetraethylorthosilicaat (TEOS) niet in staat is de vereiste functionele groepen te vormen om met de coupling agent te reageren. Maar met gedemineraliseerd water, wat vele voordelen heeft zoals geen giftigheid, gemakkelijk te hanteren, geen milieu-belasting, enz., werd een'' nieuwe route ontwikkeld. Deze technologie laat de beste polyester (PET) hechtingswaardes zien bereikt met plasma-behandeling, en de statistische onderzoeksplanning (design of experiments, DoE) test reeks laat zien welke de parameters zijn om het koord ook naar een hoog hechtingsniveau te tillen. Echter, de RFL behandelde koorden laten nog steeds de hoogste hechtingswaardes zien.

Een nadeel van deze techniek is, dat het verdere verwerking vereist na de plasma behandeling om een coupling agent te incorporeren. Helaas hebben de coupling agents in een silica-mengsel reeds gereageerd wanneer de koord-rubber binding tot stand moet worden gebracht; zij kunnen niet meer met het koordoppervlak reageren. Daardoor is een aparte koord silanisatie-stap een vereiste.

De penetratie-diepte van rubber in de koord-structuur is een van de cruciale parameters voor een goede hechting. Echter, de algemene stelling dat een penetratie-diepte van 4 filament-lagen ideaal is kon niet worden bevestigd: het gaf niet het verwachte hoogste adhesie-niveau. De kopdruk in de extruderkop bij het berubberen van het koord na de plasma-behandeling werd verwacht een significante invloed te hebben op de penetratie-diepte. Echter, in de praktijk was er geen direct verband tussen de extruder-kopdruk, penetratie-diepte en hechting: de hoogste kopdruk leidde niet tot de beste penetratie, noch hechting. Verklaringen voor dit effect zouden kunnen zijn, dat een hoge druk in de dwarse extruderkop het koord te veel samendrukken, hetgeen een diepere penetratie belemmert. Bij geoptimailiseerde extruder instellingen raakt een grote aantal filamenten gekoppeld aan de rubber, maar de hechtingsresultaten stagneren op een bepaald niveau. Dit wordt gezien als een aanwijzing, dat de plasma behandeling de dieper gelegen filamenten niet bereikt en inderdaad slechts een zuiver oppervlakte behandeling is. Een faalmechanisme wat in een vergelijkbare richting wijst met betrekking tot plasma penetratie-diepte en hechtingssterkte werd waargenomen in de zin, dat de buitenste filamenten ingebed in rubber zich afscheiden van de binnenste sectie van het koord. Dit betekent, dat de hechting tussen deze filamenten en de rubber sterker is dan hun verbinding met het binnenste van het koord.

De mechanische eigenschappen van het koord hangen in zeker mate af van de verwerkingscondities bij het opbrengen van een adhesie-promotor. Veranderingen in deze eigenschappen zoals optreden gedurende het applicatie proces van een RFL-dip, kunnen ook worden bereikt met plasma behandeling. Voor Rayon is een stikstof plasma-behandeling geschikt om de koord-eigenschappen te verschuiven naar dicht bij een RFL-gedipt koord. In geval van polyester is lucht-plasma de beste keuze om de mechanische eigenschappen te beïnvloeden. Gericht instellen van deze eigenschappen is mogelijk met een plasma-behandeling. Dit is een belangrijke factor, aangezien dit zij-effect van de hechtings-verbeterings behandeling een significante invloed heeft op RFL-gedipt zowel als op plasma-gelaagd koord, en de eigenschappen bepaalt welke in gebruik zijn bij banden-bouwen. De oppervlakte energie wordt eveneens beïnvloed door plasma-behandeling. Het effect valt meer op bij rayon koorden dan bij polyester koorden. Het effect blijkt blijvend te zijn, daar het weken aanwezig blijft na de feitelijke plasma-behandeling. Daarom is het een goede techniek om het hydrofiele karakter van rayon in te stellen. Het polyester oppervlak bewees, dat het inderdaad hoogst inert is, aangezien het niet werd beïnvloed door de plasma behandeling wat betreft de oppervlakte energie. De thermische stabiliteit van de koorden is ook een punt in het plasma behandelingsproces: polyester is gevoelig voor de warmte-blootstelling door de plasma bron. Langzaam opwinden veroorzaakte ernstige defecten op het koord oppervlak en een sterk verlies in mechanische eigenschappen.

Thermische veroudering van gevulkaniseerde H-pullout monsters in een warme oven bij 70oC toonde aan, dat alle hechtingsbevorderings systemen gevoelig zijn voor dit soort veroudering. Er is geen significant voordeel van het ene systeem over de andere. Terwijl RFL de beste initiële hechtingskracht vertoont, verliest het het meeste gedurende veroudering. Dit geldt voor beide koord-types: rayon en polyester. Over het geheel genomen is het effect van thermische veroudering op de hechtingskracht onafhankelijk van het hechtingssysteem.

Het versterkende koord werd – voor vulkanisatie van de test-monsters – ook onderworpen aan thermische veroudering. Verrassenderwijs vertoonde RFL nog steeds het beste gedrag, bij de hoogste verouderingssnelheid gedurende de eerste 24 uur. Nadien stabiliseerde het en vertoonde geen verdere achteruitgang in gedrag, voor rayon zowel als voor polyester. Het gedrag van de plasma behandelde monsters is verschillend. Waar de met thiopheen behandelde en berubberde rayon koorden een relatief langzame maar gestage achteruitgang in eigenschappen vertoonden, functioneerden de onbeschermde en niet-berubberde plasma monsters slecht na deze verouderings-condities. Zij leden aan een vroege achteruitgang in eigenschappen, welke voortzette met toenemende verblijftijd in de hete-lucht oven. Het met water behandelde polyester monster degradeerde zo heftig, dat het al z’n waardevolle effecten van de behandeling verloor. Daarom is het cruciaal dat de plasma behandeling onmiddellijk wordt gevolgd door verdere verwerkingsstappen om het effect van de plasma-behandeling te beschermen. Wanneer een beschermende laag eenmaal op z’n plaats is kan het koord worden bewaard en verder verwerkt voorafgaand aan de vulkanisatie. Het versterkende koord zelf wordt niet aangetast door thermische veroudering. Trekproeven toonden zeer stabiele resultaten in mechanische eigenschappen over de gehele test-periode. Dit laat wel zien dat de koorden verhoogde temperaturen kunnen accepteren, maar het hechtings-promotie-systeem aangebracht op het koord-oppervlak verliest een significante hoeveelheid van z’n vermogen om aan rubber te hechten naarmate de tijd coortschrijdt.

REFERENCES

1. Apollo Tyres Global R&D B.V., Enschede, The Netherlands, (2014).
2. Bekaert, Cordenka, Kordasa, Introduction to Tire Reinforcment Materials, Tyre Technology Expo, Cologne, Germany, pp. 11, (2015).
3. Bekaert, Cordenka, Kordasa, Introduction to Tire Reinforcment Materials, Tyre Technology Expo, Cologne, Germany, pp. 12, (2015).
4. W. B. Wennekes, PhD thesis, University of Twente, Enschede, The Netherlands, (2008).
5. Bekaert, Cordenka, Kordasa, Introduction to Tire Reinforcment Materials, Tyre Technology Expo, Cologne, Germany, pp. 13, (2015).
6. R. B. Durairaj, Resorcinol; Chemistry, Technology and Applications, Springer-Verlag Berlin Heidelberg, ed. 1, pp. 748, (2005).
7. B. Crowther, Handbook of Rubber Bonding, Smithers Rapra Press, pp. 398, (2001).
8. J. Kiesewetter, paper presented at the ISIFM - Meeting 2002, Atlanta, USA, (2002).
9. Formaldehyde Registration Dossier, European Chemicals Agency, ECHA, (2012).
10. Cordenka GmbH & Co KG, paper presented at the Tire Technology Expo 2015, Cologne, Germany, (2015).
11. O. D. B. Müller, paper presented at the Tire Technology Expo 2015, Cologne, Germany, (2015).
12. N. N. Cevahir, A. E. Acar, S. Bas, A dipping material for cord fabrics and a production method thereof, Patent: WO2014091376 A1, (2014).

13. T. S. Solomon, Two-step process for dipping textile cord or fabric and resorcinol/formaldehyde-free composition used therein, Patent: CA1249386 A1, (1989).

14. S. Bas, B. Ergun, A method for producing fiber reinforced rubber comprising unsaturated bonds, Patent: WO2014020570 A2, (2014).

15. Plasmatreat GmbH, www.plasmatreat.de, Steinhagen, Germany, (2005).

16. H. Conrads, M. Schmidt, Plasma generation and plasma sources. Plasma Sources Sci. T 9, pp. 441-454, (2000).

17. W. Crookes, On Radian Matter. The Popular Science Monthly 16, (1879).

18. J. M. Anderson, Irving Langmuir and the origins of electronics. IEEE Power Engineering Review 22, pp. 38-39, (2002).

19. C. Tendero, C. Tixier, P. Tristant, J. Desmaison, P. Leprince, Atmospheric pressure plasmas: A review. Spectrochim Acta B 61, pp. 2-30, (2006).

20. J. Schombert, http://abyss.uoregon.edu/~js/21st_century_science/lectures/lec05.html, Department of Physics, University of Oregon, USA, (2012).

21. M. I. Boulos, P. Fauchais, E. Pfender, Thermal Plasmas: Fundamentals And Applications, Plenum Press, New York, USA, (1994).

22. V. Sharma, S. Tiwari, B. L. Ahuja, Electronic structure, Compton profiles and cohesive properties of Cs-halides, Rad. Phys. Chem. 79, pp. 678, (2010).

23. M. D. Calzada, M. Moisan, A. Gamero, A. Sola, Experimental investigation and characterization of the departure from local thermodynamic equilibrium along a surface-wave-sustained discharge at atmospheric pressure. J. Appl. Phys. 80, pp. 46-55, (1996).

24. M. D. Calzada, A. Rodero, A. Sola, A. Gamero, Excitation kinetic in an Argon plasma column produced by a surface wave at atmospheric pressure. J. Phys. Soc. Jpn. 65, pp. 948-954 (1996).

25. J. R. Roth, Industrial Plasma Engineering, Institute of Physics Publishing, Bristol, UK, (1995).

26. A. Schütze et al., The atmospheric-pressure plasma jet: A review and comparison to other plasma sources, Plasma Sci. 26, pp. 1685-1694, (1998).

27. V. Nehra, A. Kumar, H. K. Dwivedi, Atmospheric Non-Thermal Plasma Sources. Int. J. Eng. 1, pp. 53-68, (2008).

28. F. Denes, Macromolecular plasma-chemistry: an emerging field of polymer science. Progr.Pol. Sci. 29, pp. 815-885, (2004).

29. C. S. Ren, K. Wang, Q. Y. Nie, D. Z. Wang, S. H. Guo, Surface modification of PE film by DBD plasma in air, Appl. Surf. Sci. 255, pp. 3421-3425, (2008).

30. U. Kogelschatz, Dielectric -barrier Discharges: Their History, Discharge Physics, and Industrial Applicatios, Plasma Chem. Plasma Proc. 23, (2003).

31. S. Meiners, J. G. H. Salge, E. Prinz, F. Förster, Surface modification of polymer materials by transient gas discharges at atmospheric pressure, Surf. Coatings Techn. 98, pp. 1121-1127, (1998).

32. F. O. Massines et al., Experimental and theoretical study of a glow discharge at atmospheric pressure controlled by dielectric barrier, J. Appl. Phys. 83, pp. 2950, (1998).

33. L. Bardos, H. Barankova, Cold atmospheric plasma: Sources, processes, and applications, Thin Solid Films 518, pp. 6705-6713, (2010).

34. J. L. Walsh, F. Iza, N. B. Janson, V. J. Law, M. G. Kong, Three distinct modes in a cold atmospheric pressure plasma jet, J. Phys. D. Appl. Phys. 43, (2010).

35. P.-L. Girard-Lauriault et al., Atmospheric Pressure Deposition of Micropatterned Nitrogen-Rich Plasma-Polymer Films for Tissue Engineering, Plasma Proc. Pol. 2, pp. 263-270, (2005).

36. M. Noeske, J. Degenhardt, S. Strudthoff, U. Lommatzsch, Plasma jet treatment of five polymers at atmospheric pressure: surface modifications and the relevance for adhesion, Int. J. Adhes. 24, pp. 171-177, (2004).

37. M. Laroussi, Nonthermal decontamination of biological media by atmospheric-pressure plasmas: review, analysis, and prospects, Plasma Sci. 30, pp. 1409-1415, (2002).

38. X. T. Deng, J. J. Shi, M. G. Kong, Protein destruction by a helium atmospheric pressure glow discharge: Capability and mechanisms, J. Appl. Phys. 101, (2007).

39. G. Fridman et al., Applied Plasma Medicine, Plasma Proc. and Pol. 5, pp. 503-533, (2008).

40. C.-K. Chen, W. L. Perry, H. Xu, Y. Jiang, J. Phillips, Plasma torch production of macroscopic carbon nanotube structures, Carbon 41, pp. 2555-2560, (2003).

41. C. Richmonds, R. M. Sankaran, Plasma-liquid electrochemistry: Rapid synthesis of colloidal metal nanoparticles by microplasma reduction of aqueous cations, Appl. Phys. Letters 93, (2008).

42. J. L. Walsh, J. J. Shi, M. G. Kong, Contrasting characteristics of pulsed and sinusoidal cold atmospheric plasma jets, Appl. Phys. Letters 88, (2006).

43. D. W. Liu, J. J. Shi, M. G. Kong, Electron trapping in radio-frequency atmospheric-pressure glow discharges, Appl. Phys. Letters 90, (2007).

44. D. W. Liu, F. Iza, M. G. Kong, Evolution of Atmospheric-Pressure RF Plasmas as the Excitation Frequency Increases, Plasma Proc. Pol. 6, pp. 446-450, (2009).

45. J. J. Shi, J. Zhang, G. Qiu, J. L. Walsh, M. G. Kong, Modes in a pulse-modulated radio-frequency dielectric-barrier glow discharge, Appl. Phys. Letters 93, (2008).

46. N. Balcon, A. Aanesland, R. Boswell, Pulsed RF discharges, glow and filamentary mode at atmospheric pressure in argon, Plasma Sources Sci. Techn. 16, pp. 217-225, (2007).

47. M. G. Kong, X. T. Deng, Electrically efficient production of a diffuse nonthermal atmospheric plasma, Plasma Sci. 31, pp. 7-18, (2003).

48. X. Lu, Z. Jiang, Q. Xiong, Z. Tang, Y. Pan, A single electrode room-temperature plasma jet device for biomedical applications, Appl. Phys. Letters 92, (2008).

49. X. Lu, M. Laroussi, Dynamics of an atmospheric pressure plasma plume generated by submicrosecond voltage pulses, J. Appl. Phys. 100, (2006).

50. J. L. Walsh, M. G. Kong, Sharp bursts of high-flux reactive species in submicrosecond atmospheric pressure glow discharges, Appl. Phys. Letters 89, (2006).

51. J. L. Walsh, M. G. Kong, 10ns pulsed atmospheric air plasma for uniform treatment of polymeric surfaces, Appl. Phys. Letters 91, (2007).

52. Monsanto Co., Bonding of poly(ethylene terephthalate) induced by low-temperature plasmas, Patent: US3853657 A, (1974).

53. The General Tire & Rubber Company, Adhesion of aramid cords to rubber, Patent: US4469748 A, (1984).

54. The General Tire & Rubber Company, Adhesion of rubber to aramid cords, Patent: US4680228 A, (1987).

55. Teijin Limited, Plasma and ion plating treatment of polymer fibers to improve adhesion to RFL rubber, Patent: US4756925 A, (1988).

56. The Goodyear Tire & Rubber Company., Process for the surface treatment of polymers for reinforcement-to-rubber adhesion, Patent: US5053246 A, (1991).

57. The Goodyear Tire & Rubber Company, Process for the surface treatment of polymers for reinforcement-to-rubber adhesion, Patent: US5283119 A, (1994).

58. The Goodyear Tire & Rubber Company, Process to produce reinforced tire cords with plasma treated fibers incorporated into a rubber/blocked isocyanate composition, Patent: US5501880 A, (1996).

59. Milliken & Company, Vinyl compound plasma pre-treatment for promoting the adhesion between textiles and rubber compounds, Patent: US6096156 A, (2000).

60. The Goodyear Tire & Rubber Company, Plasmapolymerisierungsdüse, Luftplasmasystem damit und Verfahren zur Abscheidung eines Polymermaterials, Patent: EP2326152 A2, (2011).

61. The Goodyear Tire & Rubber Company, Atmospheric plasma treatment of reinforcement cords and use in rubber articles, Patent: US20110241269 A1, (2011).

62. The Goodyear Tire & Rubber Company, Atmospheric plasma treatment of tire cords, Patent: EP2371882 A1, (2011).

63. The Goodyear Tire & Rubber Company, Atmospheric plasma treatment of reinforcement cords and use in rubber articles, Patent: "EP2716695 A1, (2014).

64. The Goodyear Tire & Rubber Company, Pneumatic tire and method for making a pneumatic tire, Patent: US20120067485 A1, (2012).

65. The Goodyear Tire & Rubber Company, Pneumatic tire and method for making a pneumatic tire, Patent: US20130186538 A1, (2013).

66. Westinghouse Electric Corp., Method for treating fibers, Patent: US4606930 A, (1986).

67. C. Riccardi, P. Esena, R. A. Barni, R. Siliprandi, S. Zanini, Atmospheric-plasma processing method for processing materials, Patent: US20100163534 A1, (2010).

68. Schlumberger Technology Corp., Inline plasma treatment of an optical fiber cable structure, Patent: US20120006468 A1, (2012).

69. Sigma Laboratories Of Arizona, Llc, Electromagnetic treatment in atmospheric-plasma coating process, Patent: US7557019 B2, (2009).

70. Matador Rubber, S.R.O., Method of treatment of textile reinforcing materials to increase their adhesion to rubber compound, Patent: WO2006135347 A1, (2006).

71. Matador Rubber, S.R.O., Device for manufacturing rubberized fabric cord, suitable to be used as wound overlapping breaker, Patent: WO2006088436 A1, (2006).

72. Michelin, Process for treating a body of stainless steel so as to promote its adherence to a rubber composition, Patent: EP0738748 A1 (1999).

73. P. J. de Lange, P. G. Akker, paper presented at the Tire Technology Expo 2009, Hamburg, Germany, (2009).

74. U. Kogelschatz, paper presented at the Hakone VII Int. Symp., (2000).

75. Technical University of Denmark, http://www.dtu.dk/english, Denmark, (2012).

76. Vito NV, www.vitoplasma.com, Materials Technology – Plasmazone, K-Messe (2013).

77. H. Krump, J. Hudec, M. Jasso, E. Dayss, P. Crimmann, Surface modification of PET by two different types of plasma reactors. Kautsch. Gummi Kunstst. 57, pp. 662-667, (2004).

78. E. Riedel, Anorganische Chemie, 4. Aufl., de Gruyter ;Berlin, New York (1999).

79. Sigma-Aldrich Chemie GmbH, Technical data sheet (CAS), Munich, Germany, (2017).

80. Janypka, P., et al., Method of treatment of textile reinforcing materials to increase their adhesion to rubber compound, (2006).

81. J. L. Vicario, Reactivity of heterocyclic compounds, Department of Organic Chemistry, Faculty of Science and Technology, University of the Basque Country, Spain, (2010).

82. A. L. Harreus, Pyrrole, in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, (2000).

83. H. T. Sahin, Pyrrole thin films deposited on paper by pulsed RF plasma, Cent. Europ. J. Chem., pp. 824-834, (2007).

84. L. Rupprecht, Conductive Polymers and Plastics: In Industrial Applications, Plastics Design Library, Norwich, USA, (1999).

85. Dahlmann, M., M., J. Grub, J., E. Löser, E., Butadiene, pp. 1-24, (2011).

86. Flanagan, D.W., Solid phase synthesis of graft copolymers of poly(thiophene)s and peptides containing 3-thienylalanine, University of Massachusetts Amherst. p. 215, (2004).

87. Yasuda, H.K., Plasma Polymerization, Academic Press Inc., London, (1985).

88. Shishoo, R., Plasma Technologies for Textiles, Shishoo Consulting, Sweden: Woodhead Publishing, (2007).

89. ASTM International, W.C., PA, USA, ASTM D4776 / D4776M-10, in Standard Test Method for Adhesion of Tire Cords and Other Reinforcing Cords to Rubber Compounds by H-Test Procedure. Book of Standards Volume: 07.02, (2010).

90. ASTM International, W.C., PA, USA, ASTM D4393-00, in Standard Test Method for Strap Peel Adhesion of Reinforcing Cords or Fabrics to Rubber Compounds, (2000).

91. van der Heide, P., X-Ray Photoelectron Spectroscopy: An Introduction to Principles and Practices, John Wiley & Sons, Inc., Hoboken, NJ, USA, (2011).

92. X. C. Tong, Advanced Materials for Thermal Management of Electronic Packaging, Springer Science + Business Media, New York, USA, (2011).

93. Leica Microsystems, http://www.leica-microsystems.com/science-lab/factors-to-consider-when-selecting-a-stereo-microscope/, Wetzlar, Germany, (2012).

94. N. S. Claxton, T. J. Fellers, M. W. Davidson, Laser Scanning Confocal Microscopy, Department of Optical Microscopy and Digital Imaging, The Florida State University, Tallahassee, USA, (2015).

95. Demtröder, W., Laser Spectroscopy - Vol. 2: Experimental Techniques, Springer-Verlag Berlin Heidelberg, Germany, (2008).

96. Krump, H., et al., Surface modification of PET by two different types of plasma reactors. Kautsch. Gummi Kunstst. 57, pp. 662-667, (2004).

97. Cruz, G.J., J. Morales, and R. Olayo, Films obtained by plasma polymerization of pyrrole. Thin Solid Films 342, pp. 119-126 (1996).

98. Michelin, http://www.michelin.com/eng/innovation/fields-of-innovation/tires-and-alternatives/1992-Green-tire2, Clermont Ferrand, France, (1992).

99. D. R: Lide, CRC Handbook of Chemistry and Physics, 88th Edition, CRC Press, Taylor & Francis, Boca Raton, p. 3-254, (2007).

100. H. D. Luginsland, W. Hürth-Kalscheuren, Reactivity of the sulfur chains of the tetrasulfane silane Si69 and the disulfane silane TESPD, Kautsch. Gummi Kunstst., 53, pp. 10-23, (2000).

101. A. Hunsche, U. Görl, H. G. Koban and T. Lehmann, Kautsch. Gummi Kunstst., 51, pp. 525 (1998).