

## Technologien für Kord / Gummi - Adhäsion in Reifenanwendungen

Adhäsion · Resorcinol-Formaldehyd-  
latex · RFL · Plasma-Behandlung ·  
Reifen

Die Adhäsion zwischen Gummi-Matrix und verstärkendem Kord ist ein fundamentaler Faktor für die Leistungsfähigkeit und Sicherheit eines Reifens. Üblich ist eine Resorcin-Formaldehyd-Latex (RFL) Behandlung der Korde, um die benötigte Adhäsion zu erreichen. Oft wird dabei zusätzlich eine Epoxid-Behandlung angewandt, um beide Komponenten kompatibel zu machen. Ein Überblick über diese chemischen Verfahren wird gegeben und neue Entwicklungen in diesem Themengebiet werden aufgezeigt. Umweltbedenken und neue Gefahreinstufungen erfordern sinnvolle Alternativen, weshalb in diesem Artikel aufgezeigt wird, ob und welche Alternativen anwendbar sind. Die Plasmabehandlung der Kord-Oberfläche ist dabei eine vielversprechende Möglichkeit.

Adhesion · resorcinol formaldehyde  
latex · RFL · plasma treatment · tire

A good adhesion between the rubber of a tire and the reinforcing polymeric cord is crucial for the overall tire performance and safety. Polymeric cords are commonly treated by a resorcinol formaldehyde latex (RFL) coating to obtain the desired adhesion, often in combination with an epoxy coating in order to make the cord surface and the RFL coating compatible. An overview of these chemical treatments is given, and recent developments in this field are shown. Environmental and toxicity disadvantages are the driving forces to find suitable replacements; therefore, it is discussed if the RFL treatment can be replaced and which alternative technologies might be suitable. The plasma treatment of the cord surface is one of the most promising candidates in this field.

Figures and Tables:  
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# Technologies for Polymeric Cord/ Rubber Adhesion in Applications

## Introduction

Composites made from rubber and reinforcing cords are very common and versatile goods. Well-known examples of these are car- and bicycle-tires, as well as several types of belts and hoses. Clearly, car tires are by far the most important product group within all areas of application.

Key element is the reinforcement of the 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 within the rubber matrix with only minor work required. However, the adhesion phenomenon is affected by several different types of interfacial adhesion, which all have a certain contribution to the overall resultant adhesion.

In this review, it will be discussed which adhesion types contribute in case of polymeric reinforcing cords for rubber matrices with focus on application in car tires. Furthermore, the state of the art technology will be reviewed and possible alternatives will be introduced. A comparison of these techniques is made and based on the outcome, and a final conclusion is drawn.

## Requirements for adhesion

Polymeric cords and rubber are not 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. Therefore, the physical interactions with non-polar rubber are weak. The compatibility of both materials is important in order to enable a proper wetting of the cords with rubber, which is a necessary prerequisite for adhesion phenomena like physical surface interactions, mechanical interlocking and chemical bonding. None of the cords used

for reinforcing applications feature compatibility with rubber which is sufficient without prior treatment. Therefore, a treatment of the polymeric cord is performed in order to enhance the compatibility and form a physical or chemical bond. The most common technology is the RFL technique which will be discussed later on.

The best contribution to adhesion comes from chemical bonding. It provides the strongest and most reliable adhesion between the adherent layers. Covalent chemical bonds are the strongest bonds and highly durable as well. These bonds can be established across the interface of two composite layers and, therefore, form a stable connection. A requirement for chemical bonding is that appropriate functional groups are available on both surfaces and that reaction takes place.

Besides covalent chemical bonds, also ionic bonds can be very strong. They can occur in multiple forms like ion-ion, ion-dipole or dipole-dipole bondage. By far the highest contribution to adhesion can be reached by ion-ion interactions. This type can have bonding energies of up to 450 kJ/mol [1]. The other interaction variants have much lower bonding energies as can be seen in Table I [2]. Another bond type is hydrogen bonding that occurs between e.g. hydroxyl functional groups or water molecules. The strength of hydrogen bonds is relatively low with a bonding energy of 24 kJ/mol [1].

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Adhesion caused by interfacial diffusion is a surface interaction that can build up sufficient adhesion levels, if both materials are actually compatible and well in contact. The contact interface is then crossed by molecules of both sides diffusing into each other. Unlike rapid chemical reactions or van der Waals interactions, diffusion processes are rather slow with reaction times ranging from minutes to years [3]. In case of polymeric interactions, it is reported that long-chain molecules tend to adhere better because of their ability to be present in both materials by reptation. The interfacial depth can have a range of up to 100 nm [4].

Electrostatic effects are another surface interaction that can induce adhesion. The adhesive interface can allow electron transfer if there is a dissimilar electronic structure between the materials. In particular in metal-polymer systems, this phenomenon can be an explanation for adhesion and account for the resistance to separation. However, in pure polymer composites, this effect is very weak and negligible in comparison with covalent or ionic bonds [5].

Mechanical interlocking is an important factor for adhesion too. A good example is gluing of wooden pieces, where the adhesion is mainly realized by mechanical interlocking of the glue in the rough wooden structure. In such a case the bonding strength depends on the surface roughness and the mechanical properties of the glue. Polymeric cords typically have a highly orientated, inert surface. Therefore, the contribution of the filaments to the overall adhesion between cord and rubber is minor, as they tend to easily slip out of the interlocking if a force is applied. With a high degree of branching the situation is different, but this technique is not applied in the field of cord-rubber-adhesion. That being said with respect to the exception of older use of cotton, where the main contributing factor to adhesion came from fibrillation of the cotton-fibers.

### Resorcinol Formaldehyde Latex (RFL) Systems – State of the art

A lot of rubber articles for highly demanding applications are commonly reinforced rubber/cord or rubber/steel composite materials. The reinforcement effect comes from the combination of two very different materials: On one hand the highly elastic rubber and on the other hand a cord with high strength and low elongation properties. The adhesion

**1** Typical bond energies of common bonding types [2]

Type	Example	E (kJ/mol)
Covalent	C-C	350
Ion-ion	Na <sup>+</sup> ...Cl <sup>-</sup>	450
Ion-dipole	Na <sup>+</sup> ...CF <sub>3</sub> H	33
Dipole-dipole	CF <sub>3</sub> H...CF <sub>3</sub> H	2
London dispersion	CF <sub>4</sub> ...CF <sub>4</sub>	2
Hydrogen bonding	H <sub>2</sub> O...H <sub>2</sub> O	24

**2** Typical recipe of RFL dip system for rayon cord in phr [8]

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	-
Vinyl-Pyridine-SBR-latex (40%)	212.0	84.8
Water	100.0	-
<b>TOTAL</b>	<b>500.0</b>	<b>100.0</b>

between both components of the composite is thereby the critical parameter for gaining the best overall performance for such products. The main function of a composite adhesive is to gradually transfer the load stress from the rubber matrix to the reinforcing cord. 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 stronger rayon cords and full-synthetic cords like polyester led to increased adhesion requirements and therefore to the development of new adhesives. The resorcinol formaldehyde latex (RFL) dip is a common industrial standard for about 75 years [7] already based on an aqueous dip system. The resin which is formed by the resorcinol and formaldehyde provides bonding to the cord. The latex component bonds to the rubber compound due to co-vulcanization. The term "RFL-treatment" covers a large variety of treatments. They share the same technique but differ in formulation and application. The system is adjusted to be suitable for the materials used for a specific composite, as each cord type and rubber may require different treatment conditions.

Multiple steps are required for the application of a RFL dip system. A typical recipe for such an adhesive dip is shown in Table II [8]. These values may vary within certain limits, but to simplify procedures it is convenient to use standard recipes which maintain adequate adhesion levels in several applications. Before the actual treatment of a cord can be

executed, the preparation of the RFL dip system has to be done. It consists of two major production steps; in a first step resorcinol is dissolved in water to obtain an aqueous solution. Subsequently formaldehyde and sodium hydroxide as condensation catalyst are added with the aim to form methanol groups (resole) on the resorcinol.

This mixture is stirred for 6 hours at room temperature to form a resin solution. The second step is the introduction of the latex: Under gentle stirring the resin is added to the latex to ensure good mixing of the dip system [8]. Finally this "dip solution" is allowed to mature for 24 hours before further use. The final dip properties are shown in Table III. An increase of formaldehyde concentration increases the rate of methanol-group formation. The optimal formaldehyde to resorcinol ratio is about 2 to 1, and yields a complete methanol reaction. Furthermore, the formaldehyde concentration increases the viscosity of the resin because of the formation of higher molecular weight products [6].

In the case of polyamide or rayon cords, a standard treatment with RFL dip is sufficient, as the reactivity of these cords is high enough. A condensation reaction between the resin (resole) and the polymeric cord takes place, see Figure 1 for an example with nylon cord. The dipping process is straight forward, as the cords are dipped with the RFL solution and the deposited layer is then dried and cured by exposure to heat. Commonly, a treatment time of 1 to 2 minutes at a temperature in



3 Final dip properties of a typical formulation [6]		
Properties	Value	Parts (dry)
Dip solids (%)	18-26	9.4
pH	9 to 10	5.1
Formaldehyde/resorcinol molar ratio	2/1	0.7
Resin/latex ratio	15-20/100	-

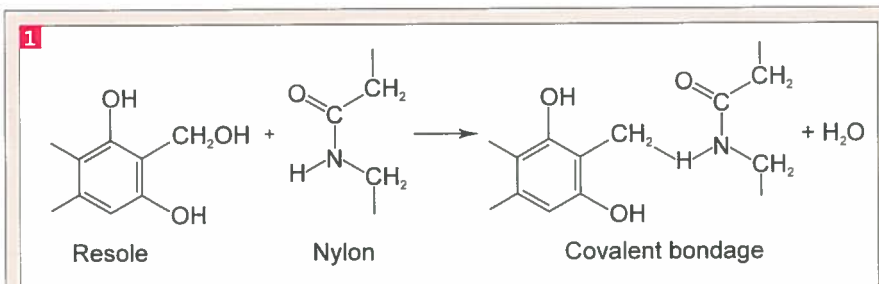


Fig. 1: Reaction scheme of a resole and nylon molecule forming a covalent bond [6].

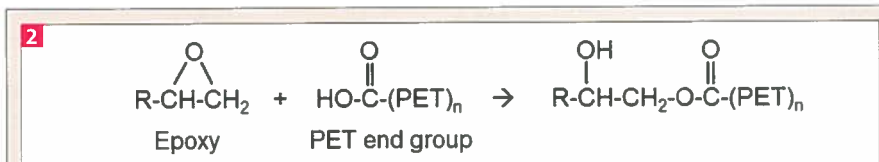


Fig. 2: Reaction scheme of a resole and nylon molecule forming a covalent bond [6].

the range between 130 °C and 150 °C is sufficient to achieve good adhesion levels.

In general it can be said, that the RFL dip systems still deliver a very good performance for adhesion promotion between rubber and reinforcing cords. That is the main advantage of this treatment, but it also shows some drawbacks, which are the driving forces to substitute the RFL treatment by alternative techniques. These drawbacks are in first instance environmental and health aspects caused by the use of toxic chemicals, as well as the multistep processing that is costly and requires time and effort. In particular formaldehyde is a problematic key ingredient, as it is now reclassified by the European Committee of Risk Assessment (RAC) to be carcinogenic (1B) and mutagenic (2) [9]. A restriction on the use of formaldehyde might be possible within Europe in the future.

Most polymeric cords feature a highly inert surface which makes them unreactive - not only towards rubber, but also towards the RFL coating. In such a case no adhesion promotion is observed. An intermediate layer - a sub-coating - is necessary, that reacts during the drying process with the cord surface and later on in a second step with the RFL top coating.

In case of polyester (PET) and aramid cords, the use of epoxides as intermediate layer is common as it results in sufficient adhesion. The epoxy-group reacts with the functional groups on the polymer backbone of e.g. aramid, or with the end groups of a polymer chain in polyester. A schematic drawing of such a reaction is shown in Figure 2.

If these reactions occur with the end groups of the polymer chains of the cord, the molar mass of the chains affects the

adhesion between cord and subcoating: the molar mass determines the number of end groups which are available for such a reaction. However, there is an excess of epoxy groups in the sub coating compared to the number of reactive functional groups on the cord surface. The unreacted epoxy groups react later on with the RFL top coating. The reaction is shown in Figure 3.

The epoxy groups may form hydroxy-ether structures with the resorcinolic hydroxyl groups of the RFL. Via this approach, the epoxy groups form chemical bonds with both, the cord surface and the RFL-coating. This is followed by the reaction of the RF-resin with the rubber compound (Figure 4). Overall, this system creates good adhesion levels with chemical bonds through three different interfaces.

A very interesting aspect of the cross-linking between rubber matrix and the RFL latex is the high affinity of the RFL dip towards the sulfuric accelerator molecules. This was demonstrated by Wennekes [7], who did SEM-EDX linescans of the RFL-rubber-interface. A high number of sulfur counts was found in the latex phase of RFL: The accelerator migrates from the rubber phase during vulcanization (Figure 5) as the RFL initially does not contain any sulfuric components. The adhesion is significantly influenced by these migrating accelerator components of the rubber compound. The affinity towards polymeric or cyclic sulfur molecules is only moderate. Furthermore, an inverse correlation between the atomic sulfur content in the RFL dip near the actual interface and adhesion was observed.

### Alternative Techniques

A detailed understanding of the RFL-technique raises the question, which kind of alternatives may be of interest for a potential replacement. Clearly, modification of the cord surface properties is the key element here with the aim to establish a method which enables covalent bonds between cord and rubber matrix. This can be done during the production of the cord in such a way, that functional groups become available on the cord surface, or via chemical post-production treatments. Such a treatment should not affect the bulk properties of the cord and, to be a valid alternative, should preferably add a significant advantage over the existing state of the art technology.

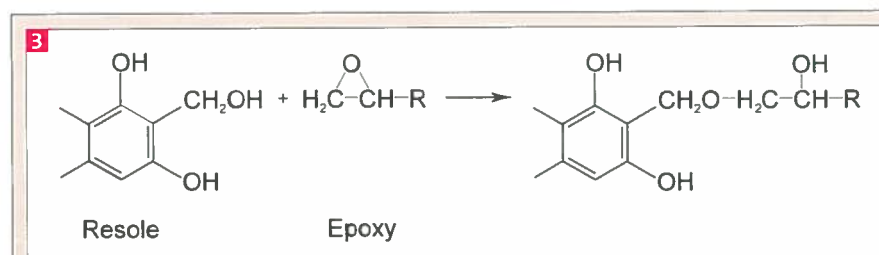


Fig. 3: Reaction scheme of a resole and nylon molecule forming a covalent bond [6].

### Alternative dipping systems

A first approach to find alternative solutions within the field of chemical treatments is in fact the use of similar treatments like RFL, but using alternative chemicals. The difficulty of this approach is to replace the problematic chemicals by health- and environmentally-friendly ones. Doing so has the advantage, that the existing processing equipment could be used without major investment costs. However, besides tailored variants of the RFL technique for each cord or application, no major innovations were introduced in this field. Attempts were taken to reduce the amount of resorcinol and formaldehyde in the resin [6]. The problem thereby is that these measures negatively affect the adhesion strength, which of course is not desired.

Recently, a RF-free dip solution for nylon cords was introduced onto the market [10]. The intention is to completely avoid the classical resorcinol formaldehyde chemistry, but still use the established dipping bath concept. Therefore, the processing steps are similar and an aqueous system, which has the advantage of good wetting ability of the cord, is used too. According to the corresponding patent [11], an acrylic resin is dissolved in water and a certain pH-value is set. The following components are added stepwise: epoxy, polyisocyanate and latex. The result is a dipping solution, which can be applied in the usual way. This dip-type is claimed to be not as hazardous as RFL for human health and to be more environmentally friendly. Clearly, the epoxy and isocyanate groups are responsible for the interaction with the cord, while the latex responds to the vulcanization process of the rubber matrix. In fact, the acrylic-resin takes over the role of the RF resin. Instead of the typical brownish finish of RFL, the RF-free dipping has a whitish appearance. In general, the mechanical properties of the RF-free dipped materials are comparable or higher than RFL-treated ones, but in particular the fatigue adhesion performance is reported to be improved [10].

### Modified fibre-polymers

Using unsaturated bonds within the chain backbones of the cord-polymer, which can form covalent bonding between the cord and the rubber matrix, was recently patented [12]. The unsaturated moieties are added during the synthesis of the polymer. The condensation comprises the reaction of diamines and dicarboxylic (nylon) or dihydroxylic acids

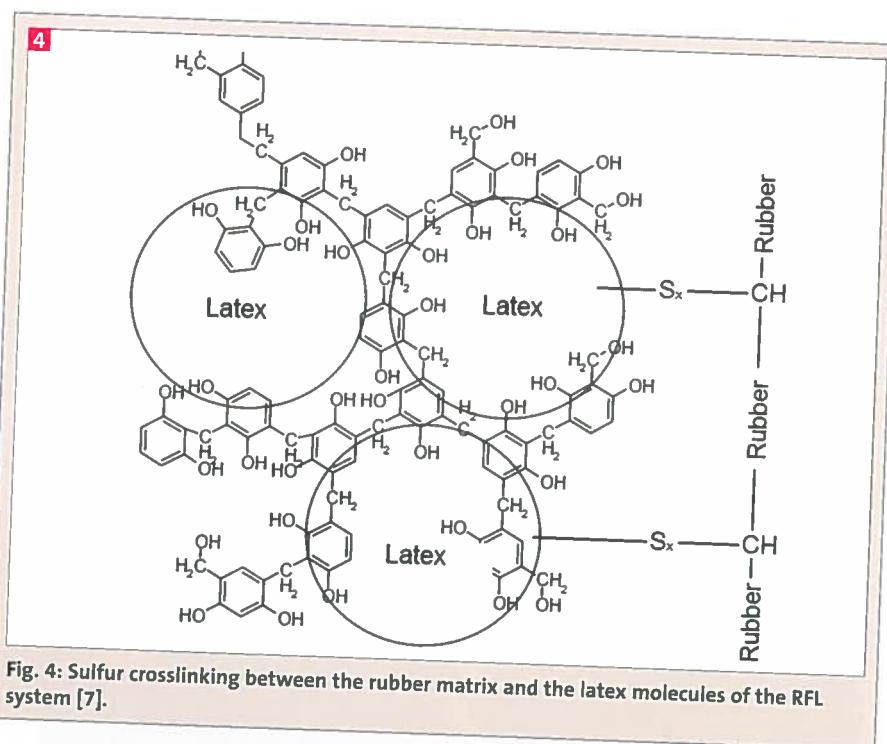


Fig. 4: Sulfur crosslinking between the rubber matrix and the latex molecules of the RFL system [7].

(polyester), in which unsaturated bonds are added in each case through linear or cyclic dicarboxylic acids. According to the patent, the amount of unsaturation can be scaled freely and, therefore, be adjusted to the amount necessary for the application. However, unlike chemical surface treatments, this method definitely changes the material properties of the polymeric cord. This significant disadvantage is counteracted by the fact, that this method makes dipping processes completely unnecessary. Besides, as it can reduce production time and effort and doesn't require expensive chemicals for the dipping process, an introduction into the market is probable. In contrast to the traditional RFL technique, this adhesion system misses the intermediate layer of a

dipped resin, and the transition of forces from the stiff cord material to the elastic rubber compound is much steeper. The chemical reaction between rubber matrix and the cord is shown Figure 6.

### Plasma treatment

Another interesting alternative is plasma treatment. It is the subject of many articles nowadays, covering a large variety of possible applications. There have been numerous attempts to improve the adhesion between cord and rubber matrix; many of them more or less successful. However, first trials based on vacuum systems require batch-wise treatment cycles, which are not desirable for industrial purposes. That is the reason why the focus shifted to atmospheric plasma sys-

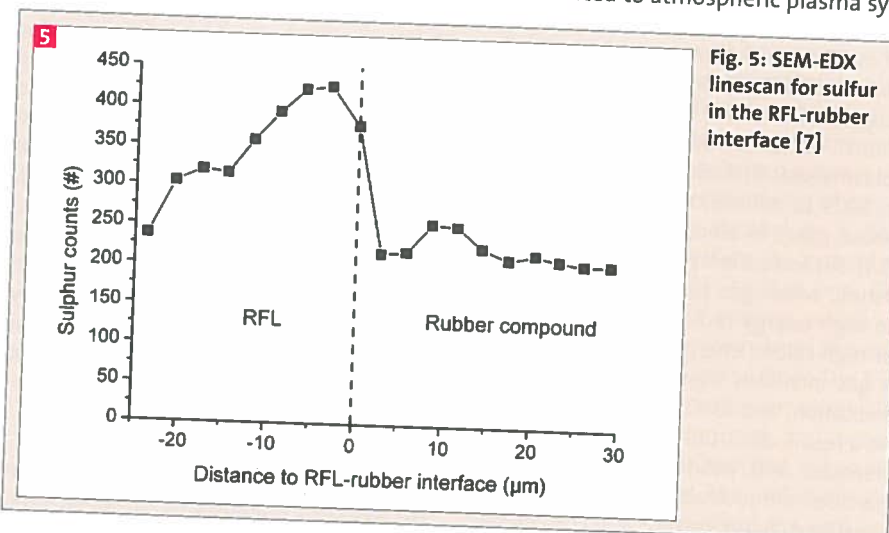
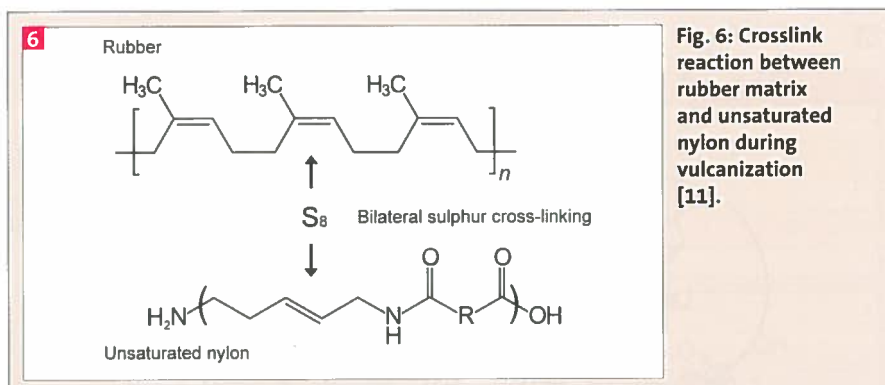
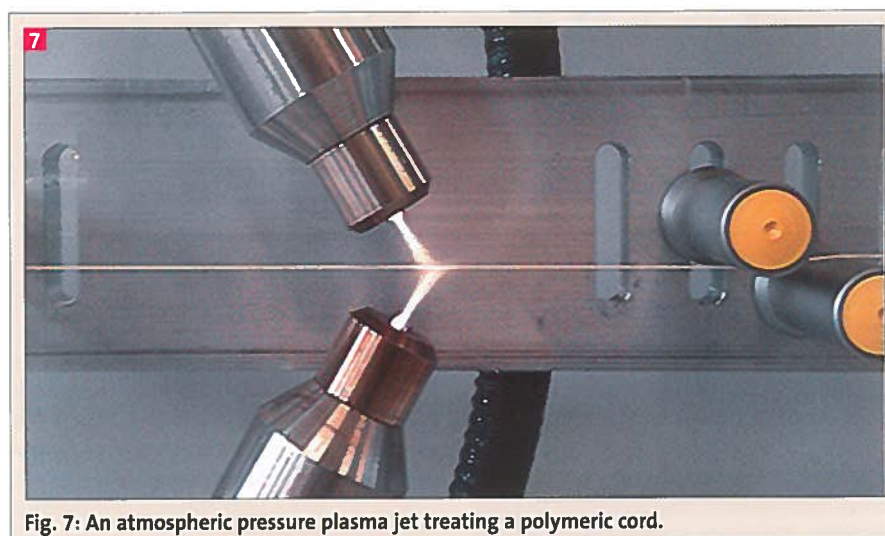


Fig. 5: SEM-EDX linescan for sulfur in the RFL-rubber interface [7]





**Fig. 6: Crosslink reaction between rubber matrix and unsaturated nylon during vulcanization [11].**



**Fig. 7: An atmospheric pressure plasma jet treating a polymeric cord.**

tems, which can be installed in a continuous line similar like a dipping bath in case of dipping systems.

The application of plasma treatment within the field of adhesion und coating technology is well known and subject of many research projects. Plasma is an extremely high energy state of a gas, in which a variety of oppositely-charged particles caused by ionization is present, while it has an overall electrically quasi-neutral charge. It is considered as a state of matter, which is much higher activated than a solid, liquid or gas state. Sir William suggested in 1879, that this state is the 'fourth state of matter' [13]. The term 'plasma' was first used by Irving Langmuir in 1929 to denote this state in an article about gases in electrical discharge tubes [14]. An ionization process can be established, when gas particles are subjected to high energy radiation, electrical fields or high caloric energy. The energy level in a gas increases significantly by external excitation, and ionization can take place. As a result, electrons of the gas atoms are released and positively charged heavy particles are produced. Thus plasma contains free charge carriers and is an electri-

cally conductive as well as 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 been converted to ions by excitation.

While in the past the focus was on vacuum plasma that was actively used by scientists, the focus shifted in the last decade to atmospheric plasma that made in particular industrial applications possible. It is a versatile tool which can be used for cleaning, etching, activating and coating applications. Plasma devices are available in several configurations, best known are atmospheric pressure plasma jets (APPJ) or dielectric barrier dischargers (DBD). An example for an APPJ treating polymeric cord is shown Figure 7. Common for these technologies is the use of air as ionization gas, because it is inexpensive, safe, easy to supply and suitable for most industrial applications. However, other ionization gases can be hydrogen, oxygen and nitrogen, as well as noble gases.

For the improvement of adhesion between polymeric cords and a rubber matrix, two plasma approaches are of interest.

The first possibility is the use of plasma in a cleaning and activation step to enhance the reactivity of the cord surface towards a dipping step. Surface cleaning is a process that is commonly performed with inert gases, as chemical modification of the surface is not desired. The aim is to remove contaminants from the substrate surface. Possible contaminants are for example oil, dust, oxides, biological and chemical agents. Metastable energetic particles are suspected to be responsible for the destruction process of contaminants. Surface cleaning is an important factor and in most cases necessary before proceeding with additional steps.

In the case of surface activation, the aim is to modify the surface energy of a substrate in order to reach a specific surface property and thus make it receptive for a certain reaction. Usually this is done with oxygen groups as they introduce polar and hydrophilic moieties which increase the material's surface energy. This effect is used for painting, printing, coating or bonding processes. Another possibility is a surface modification in which fluorination of the substrate surface creates anti-adherence properties by lowering the surface energy [15].

Another possibility is a plasma surface coating. This is a deposition process, which adds a new surface layer to the substrate and thereby changes the functionality of the substrate surface while the bulk properties remain unchanged. Of particular interest is plasma enhanced chemical vapor deposition (PECVD), as it allows plasma polymerization. A precursor is vaporized and then fed into a plasma chamber, where the substrate's surface is treated with the precursor in the plasma stream. The plasma acts here as a chemically active media and activates coating reactions. The activated precursor molecules get in contact with the substrate surface and react with it to form a coating layer. Two modes of introducing the precursor are possible. In the direct mode, the precursor is mixed with a carrier gas before being fed into the plasma chamber. This can cause a complete atomization of the precursor molecules, as the high energy particles of the plasma separate the molecules into ions. In the remote mode, the precursor is fed inside a reaction chamber into the afterglow of the plasma, which contains less reactive particles. The partially (but randomly) broken precursor is then able to introduce new functional groups onto the substrate surface [16].

In literature, the aim of using the plasma technique is twofold: either the ambition is to replace RFL completely or to reduce the number of dipping steps by replacing the epoxy sub-coating by a plasma surface activation. Van Ooij et al. [17] applied plasma treatment to untreated aramid and polyester cords. The ionization gas was argon and the precursors were pyrrole and acetylene. Enhancements of the H-pullout forces as well as improved adhesion to rubber compounds and epoxy adhesives were found, in particular if acetylene as precursor was used. Only activating these cords was not successful and did not improve the adhesion, but it was not harmful either. Hudc et al. [18 - 23] worked with untreated polyester cords and a plasma reactor using nitrogen as ionization gas. Cleaning of the cord with acetone before the plasma treatment was found to be beneficial for the adhesion. Overall, the plasma surface activation with nitrogen was reported to be very successful and the adhesion level was comparable to the level of RFL-coating. The plasma modified surface did not undergo aging when it was exposed to air before further processing. The use of a maleic acid bath after the treatment to establish grafting onto the polyester surface had no significant effect, neither had the addition of butadiene to the nitrogen ionization gas a significant effect on the adhesion.

De Lange et al. [24] compared oxygen and nitrogen plasma versus chemical treatment with the aim to replace the epoxy coating by plasma in the case of aramid cord. It was concluded, that the introduction of hydroxyl-groups was the key element for the adhesion with the resin of RFL. The number of hydroxyl-groups created by both plasma treatments was lower than in case of an epoxy-layer. Therefore, plasma treatment could not generate an improved adhesion level.

The industry contributed as well to the developments in the field of plasma treatment with focus on reinforcing cords for rubber reinforcement. Back in the 1990's, different studies were carried out to enhance the adhesion of the RFL-coating by a CF<sub>4</sub>/O<sub>2</sub> plasma treatment [25, 26]. Another approach was to use a vinyl-compound in combination with a plasma treatment [27] followed by a RFL dip. Currently the aim is clearly to use a plasma treatment alone as a replacement for the RFL technique. Examples are the application of an atmospheric plasma with a gas mixture of propane,

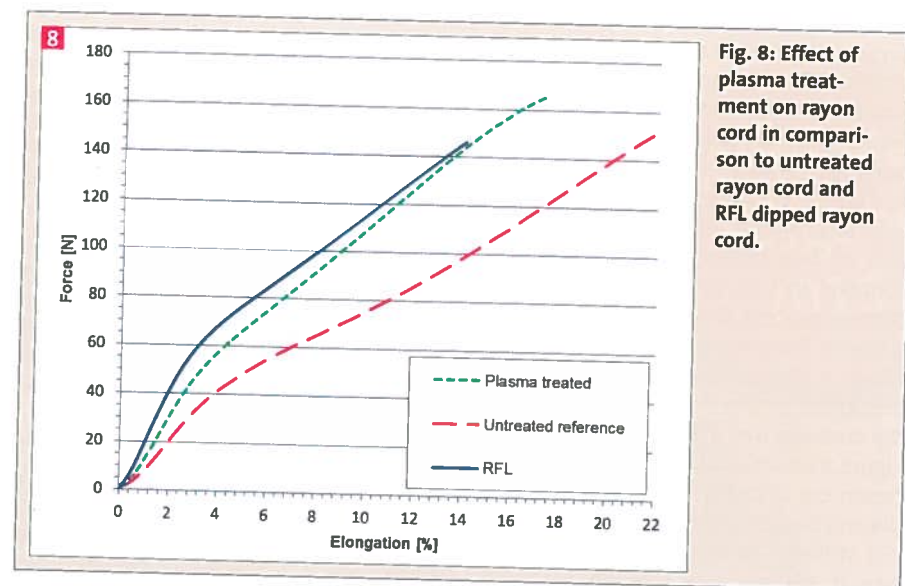


Fig. 8: Effect of plasma treatment on rayon cord in comparison to untreated rayon cord and RFL dipped rayon cord.

butane and nitrogen [28] or the plasma treatment with an atomized mixture comprised of a polymerizable monomer, a halogenated saturated hydrocarbon and a carrier gas [29]. All these approaches show that plasma treatment has the potential to be a suitable solution for the replacement of the RFL treatment.

### Comparison and Outlook

Each type of adhesion promotion technique has its advantages and disadvantages, in particular the RFL industrial standards. The RFL-coating is well established and delivers a good adhesion performance resulting in high quality products. Therefore, it fulfills the main requirements and justifies its position in the market, even though the disadvantages are significant. The dipping process itself is here the main issue: The production requires a relatively high effort, as two dipping steps are necessary, which means that high costs for equipment and production have to be taken into account. Furthermore, the health issues of the resins used nowadays require an extra effort in terms of protective measures in the production facilities. Disposal of chemical waste is another major cost factor due to their environmental burden. However, RFL-coatings are still mainly used due to the fact that almost all current products on the market are based on the properties defined by RFL-coated reinforcing cords.

The application of RF-free dips has one significant advantage over RFL: As described above, the acrylic resin recipe is less toxic and therefore much less critical to be used in production. This simplifies production procedures as less pre-

caution measures are necessary. However, besides reducing this specific health risk, the RF-free dip technology is comparable to the RFL-technique and is still using problematic chemicals which cause an environmental burden. Besides, a significant reduction in the product price is not expected, and it is likely that RF-free cords need to match the properties of the RFL-treated cords closely. Otherwise, a direct replacement would not be possible, as e.g. the construction of the tire needs to be adjusted as well.

A no-dip solution is a radically different approach compared to the two previous ones. In fact it is an innovative solution, as it solves the problem at its origin. While using a multiple dip system is rather a work-around solution to gain adhesion, the idea of adding unsaturated monomers in the cord-polymers is a direct way of getting adhesion. Therefore, it will be a major simplification as it reduces the number of processing steps and completely avoids additional chemicals. Therefore, less energy is used and there is no health issue or environmental burden. However, it is a question how complicated it is to add unsaturated bonds to the polymer. This has to be balanced against the advantages of less processing steps. A disadvantage of this technology is, that the cord-rubber-interface is completely different from the RFL-treated one: The resin-latex coating is missing, which results in a steep transition from the stiff cord to the highly elastic rubber. The RFL-coating with its intermediate properties forms a good transition zone, and there is no equivalent when applying a non-dip adhesion technology. The added unsaturated bonds will also affect the cord pro-



erties, as they are attached to the main chains of the polymer. This change in cord properties will most likely make adjustments necessary to the material specifications by the manufacturers.

Plasma treatment is an innovative way to promote adhesion. The application of this technique is efficient and compact in size, compared to a double dipping process. Due to the high temperature in the plasma zone it is possible to create a similar effect on the bulk cord properties as the drying step of the RFL dip coatings has. This effect is shown in Figure 8 which was obtained after an APPJ-treatment of rayon cord [30]. Clearly, the plasma treated rayon cord has an increased stiffness compared to an untreated one. It is likely that this effect can be used in a tailored way in an industrial plasma setup to achieve the desired bulk properties of the cord. The additional stiffness at lower elongation of RFL-treated rayon cord compared to the plasma treated one is also defined by the properties of the RFL-dip, where the resin affects the behavior of the cord as well.

Taking this into account, the plasma treatment technology has the potential to simplify the production process as well. However, it still generates exhaust gases, in particular when precursors are used for plasma coatings. The use of these chemicals requires proper venting systems and filters. An advantage is that a significantly reduced amount of chemicals can be used in a very efficient way and, therefore, the environmental burden is reduced.

Similar to the no-dip solution, the intermediate RFL-coating layer is missing in case of plasma treatment. The plasma polymerized coating layer is in fact only a few micrometers thick and cannot act as a transition zone between cord and rubber properties. A schematic drawing of the different coating types achieved by RFL and plasma technique is shown in Figure 9. When the plasma coating reacts with the rubber matrix, the bond is rather

a direct bond between cord and rubber. It is to note, that the plasma treatment only affects the surface which is accessible by the plasma. Therefore, an untreated zone inside the cord remains where single filaments of the cord fail to participate in crosslink reactions during vulcanization. The response of a plasma coated composite will differ in properties, caused by the above-mentioned lack of a transition layer with intermediate properties. Another difference is that filaments are only partly plasma coated which is caused by the twisted structure of the cord and results in different properties in the finished composite. Due to the twist of the cord, the filaments are only partly present on the surface over the whole distance. As a consequence, filaments of the cord are not completely plasma treated and later on do not entirely adhere to the rubber matrix by crosslinks. This results in a higher mobility of the single filaments alongside the cord when forces are applied. As a matter of fact, the properties of such a plasma treated cord differ in comparison to dipped cord. Further research has to determine, if this is acceptable and how this may affect aging behavior.

#### References

- [1] W.D. Callister, *Material Science and Engineering – An Introduction* (2007), John Wiley & Sons, New York, NY, USA.
- [2] S. Ebnesaajjad, C. Ebnesaajjad, *Surface Treatment of Materials for Adhesive Bonding* (2nd Edition) (2014), Elsevier Inc, Norwich, NY, USA.
- [3] D.Y. Wu, S. Meure, D. Solomon, *Prog. Polym. Sci.* 33 (2008) 479.
- [4] E.M. Petrie, *Plastics and Elastomers as Adhesives* (1975), Handbook of Plastics and Elastomers, McGraw-Hill, New York, NY, USA.
- [5] A.D. Roberts, *Adhesion* 1 (1977) 207.
- [6] R.B. Durairaj, *Resorcinol - Chemistry, Technology and Applications* (2005), Springer, Berlin, Heidelberg, Germany.
- [7] W. B. Wennekes, J. W. M. Noordermeer, *Rubber Chemistry and Technology* 80 (4), 545 (2007).

- [8] C. Crowther, *Handbook of Rubber Bonding* (Revised Edition) (2003), Rapra Technology Limited, Shropshire, UK.
- [9] RAC adopts seventeen scientific opinions, European Chemicals Agency (2012), 14 December 2012, [http://echa.europa.eu/view-article/-/journal\\_content/c89bdb13-09e9-497c-8e73-ddae13a842c8](http://echa.europa.eu/view-article/-/journal_content/c89bdb13-09e9-497c-8e73-ddae13a842c8), Helsinki, Finland.
- [10] N. Cevahir, A. Sen, *Global Tire Report* 28 (2013) 115.
- [11] WO Pat. 091376A1 (2014) to Kordsa Global Industry, Istanbul, Turkey, inv.: A.F. Mahalle-si, S. Caddesi.
- [12] WO Pat. 020570A2 (2014) to Kordsa Global Industry, Istanbul, Turkey, inv.: A.F. Mahalle-si, S. Caddesi.
- [13] S. Eliezer, Y. Eliezer, *The Fourth State of Matter: An Introduction to Plasma Science* (2nd Edition) (1989), The Institute of Physics, London, UK.
- [14] I. Langmuir, L. Tonks, *Phys. Rev.* 34 (1929) 876.
- [15] M. Schwartzman, S.J. Wind, *Nanotechnology* 20 (2009) 145306.
- [16] U. Kogelschatz, *Plasma Phys. Control. Fusion* 46 (2004) B63–B75.
- [17] W.J. van Ooij, S. Luo, S. Datta, *Plasmas and Polymers* 4 (1999) 33.
- [18] H. Krump, I. Hudec, M. Jasso, E. Days, P. Crimman, *Kautschuk Gummi Kunststoff* 54 (2004) 662.
- [19] Jasso, M., Hudec, I., Alexy, P., Kovacic, D., Krump, H., *International Journal of Adhesion & Adhesives* 26 (2006) 274.
- [20] H. Krump, I. Hudec, M. Jasso, E. Days, A.S. Luyt, *Applied Surface Science*, 252 (2006) 4264.
- [21] M. Jasso, H. Krump, I. Hudec, P. Stahel, D. Kovacic, M. Sira, *Surface & Coatings Technology* 201 (2006) 57.
- [22] H. Krump, M. Simor, I. Hudec, M. Jasso, A.S. Luyt, *Applied Surface Science* 240 (2005) 268.
- [23] I. Hudec, M. Jasso, M. Cernak, H. Krump, E. Days, V. Suriova, *Kautschuk Gummi Kunststoffe* 58 (2005) 525.
- [24] De Lange, P.J., Akker, P.G., *J. Adhesion Sci. Technol.*, 26 (2011) 827.
- [25] US Pat. 5053246 (1990) to The Goodyear Tire & Rubber Company, Akron, USA, inv.: D. Shuttleworth,
- [26] US Pat. 5283119 (1991), The Goodyear Tire & Rubber Company, Akron, USA, inv.: D. Shuttleworth.
- [27] US Pat. 5501880 (1994) The Goodyear Tire & Rubber Company, Akron, USA, inv.: D. Parker.
- [28] P. Janyпка, WO Pat. 135347A1 (2006) to Matador A.S., Púchov, Slovakia.
- [29] F. Siffer, J. Gillick, US Pat. 0241269A1 (2011) The Goodyear Tire & Rubber Company, Akron, USA.
- [30] A. Louis, W.K. Dierkes, J.W.N. Noordermeer, unpublished results.

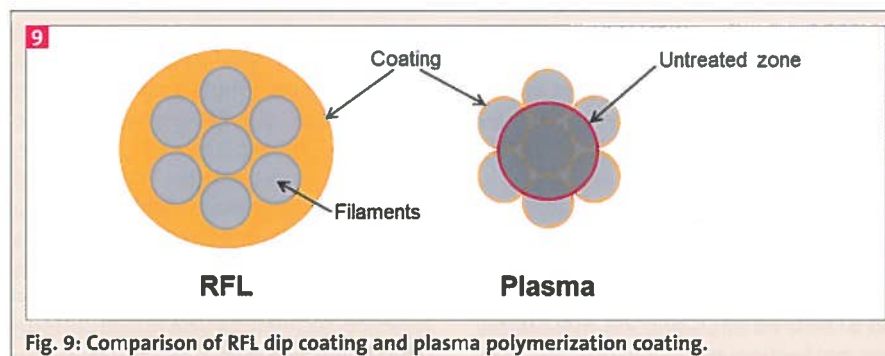


Fig. 9: Comparison of RFL dip coating and plasma polymerization coating.