TECHNOLOGIES FOR POLYMERIC CORD / RUBBER ADHESION IN TIRE APPLICATIONS

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ABSTRACT

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 in order to obtain the desired adhesion. This is often done in combination with an epoxy coating in order to compatibilize the cord surface and the RFL coating.

An overview of these chemical treatments, which are dating back to the year 1938, is given, and recent developments in this field are shown. Economical and environmental disadvantages are the driving forces to find suitable replacements, and it is discussed, if one or both chemical treatments can be replaced and which technologies might be suitable.

Plasma treatment is one of the most promising candidates, in spite of the fact that it creates different surface and core properties. One major difference is the presence of the latex in the RFL coating, which provides a chemical link between the cord and the rubber matrix, thus the plasma treatment has to provide moeities which can couple the cord to the rubber. Another difference is the thermal impact of the plasma treatment, which influences the basic properties of the cord. Besides, the state-of-the-art is plasma treatment of single end cords, which has to be further developed for multiple cords.

In this overview, chemical and mechanical aspects as well as processing of treated polymeric cords will be discussed. New approaches in this research field are shown and compared.

INTRODUCTION

Composites made of rubber and reinforcing cords are very common and versatile goods. Well-known examples of these goods 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 at all to the composite performance, as it will simply slip in 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 observed adhesion.

In this review, it will be discussed which adhesion types contribute in case of polymeric reinforcing cords for rubber matrixes with focus on applications for 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 a final conclusion is given.

REQUIREMENTS FOR ADHESION

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. Therefore, the interactions with non-polar rubber are weak. The compatibility of both materials is important in order 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: A modification 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 main 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 layers and, therefore, form a stable connection between them. A requirement for chemical bonding is that appropriate functional groups are available on both surfaces and that the reactions get initiated.

Besides chemical bonds, also physical bonds can be very strong. In particular ionic bonding that occurs 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 (see Figure 1a [1]). This type can have bonding energies of up to 450 kJ/mol. The other interaction variants have much lower bonding energies which can be seen in Table I [2]. Another physical bond type is the hydrogen bonding that occurs between e.g. hydroxyl

functional groups or different water molecules (Figure 1b [1]). The strength of hydrogen bonds is relatively low with a bonding energy of 24 kJ/mol.

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 their ability to be present in both materials is higher. The diffusive interfacial area can have a thickness of up to 1000 Å [4].

Electrostatic effects are another surface interaction that can induce adhesion. The adhesive interface can allow an 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 will be very weak and negligible in comparison to covalent or ionic bonds [5].

Mechanical interlocking can be another important factor for adhesion. A good example is the 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 bondage 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 slip out of the interlocking easily if a force is applied. With a high degree of branching the situation is a different one, but this technique is not applied to the field of cord-rubber-adhesion.

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 the one hand a highly elastic rubber and on the other hand a cord with high strength and low elongation properties. The adhesion between both components of the composite is thereby the critical parameter for gaining the best overall performance from such products. The main function of a composite adhesive is to 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 resin/latex (RFL) dip is a common industrial standard for now about 75 years [7] 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 their recipe and application. This implies that the system is adjusted to be suitable

for the materials used for a specific composite, as each cord 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, where 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).

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 also increases the rate of methanol 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 nylon or rayon, 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 2 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 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 delivers the best results for adhesion promotion between rubber und reinforcing cords. This is the main advantage of this treatment, but it also shows some drawbacks, which are the driving forces to substitute the RFL treatment with alternatives. These drawbacks are in first instance the multistep processing that is costly and requires time and effort, as well as environmental and health aspects caused by the use of toxic chemicals. Even though nowadays industrial setups provide high protection standards for workers and environment, the residues from RFL dip processing still has to be handled as special waste.

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 the second drying step with the RFL top coating.

In case of polyester (PET) and Aramid, 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. nylon, or with the end groups of a polymer chain (polyester). A schematic drawing of such a reaction is shown in Figure 3.

If these reactions occur with the end groups of the polymer chains of the cord, the molar mass of the chains affect the adhesion between cord and sub coating: 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 functional groups on the cord surface. The non-reacted epoxy groups react later on with the RFL top coating. The reaction is shown in Figure 4.

The epoxy groups may form hydroxyether 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. Later on the RF resin reacts further with the rubber compound (Figure 5). Overall, this system creates good adhesion levels with chemical bonds through three different interfaces.

A very interesting aspect of the crosslinking between rubber matrix and the RFL latex is the high affinity of the RFL dip towards the sulphuric accelerator molecules. This was found by Wennekes [7], who did SEM-EDX linescans of the RFL-rubber-interface. A high number sulphur counts was found in the latex phase of RFL. The accelerator migrated from the rubber phase during vulcanization (Figure 6) as the RFL initially does not contain any sulphuric components. The adhesion is influenced significantly by these migrated accelerator components of the rubber compound. The affinity towards polymeric or cyclic sulphur molecules is only moderate. Furthermore, an inverse correlation between the atomic sulphur 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, a 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 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 add a significant advantage over the existing state of the art technology.

ALTERNATIVE DIPPING SYSTEMS

A first approach to find alternative dipping solutions within the field of chemical treatments is in fact the use of similar treatments like RFL, but using modified 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 on 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, Kordsa Global (TR) introduced a RF-free dip solution for Nylon cords to the market [9]. 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 [10], 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 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 isocyanates 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. It is reported, that the dip pick-up is lower compared to RFL for a similar adhesion level. In general the mechanical properties of the RF-free dipped materials are comparable or higher than RFL-treated ones, in particular the fatigue adhesion performance is reported be improved [9].

MODIFIED FIBRES

Using unsaturated bonds within the backbone chains of the cord-polymer which can form covalent bonding between the cord and the rubber matrix was recently patented [11]. The unsaturated molecules are added during the synthesis of the polymer. The condensation comprises the reaction of diamines and dicarboxylic acids (nylon) or dihydroxylic acids (polyester), in which the 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. It will be seen, if this solution enters the market and can satisfy with its performance. However, as it can reduce production time and effort and doesn't require expensive chemicals for the dipping process, an introduction to the market is probable. Compared 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 more steep. The interface is illustrated in Figure 7, where the chemical reaction between rubber matrix and the cord is shown as well. Clearly, the amount of chemical groups involved to establish adhesion is greatly reduced.

PLASMA TREATMENT

Another interesting alternative is plasma treatment. It is the subject of many articles nowadays, covering a huge 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 systems, which can be installed in-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' [12]. The term 'plasma' was first used by Irving Langmuir in 1929 to denote this state in an article about gases in electrical discharge tubes [13]. 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 due to an 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 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 been converted to ions by excitation.

While in the past the focus was on vacuum plasma which has been 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 realizations, best known are atmospheric pressure plasma jets (APPJ) or dielectric barrier dischargers (DBD). Pictures of these two technologies are shown in Figure 8 a and b [14], respectively. 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 the noble gases.

For the improvement of adhesion between polymeric cords and a rubber matrix, two plasma approaches are interesting. 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. Below are brief descriptions of both steps:

Surface cleaning is a process that is commonly performed with inert gases, as a 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 a fluorination of the substrate surface creates anti-adherence properties by lowering the surface energy.

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 the plasma enhanced chemical vapor deposition (PECVD), as it allows plasma polymerization. A precursor is vaporized or atomized and then fed into a plasma chamber, where the substrate's surface is treated. 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 a direct mode, the precursor is mixed with a carrier gas before being fed into the plasma chamber. This leads to an complete atomization of the precursor molecules, as the high energy particles of the plasma separate the molecules into ions. In a remote mode, the precursor is fed into a reaction chamber in 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.

In the literature, the aim of using plasma technique is ambivalent: either the ambition is to replace RFL completely or to reduce the number of dipping steps by replacing the epoxy coating by a plasma surface activation. Van Ooij et al [15] 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 didn't improve the adhesion, but it wasn't harmful either. Hudec et al [16 – 21] worked with untreated polyester cord and a plasma reactor using nitrogen as ionization gas (Figure 9). Cleaning of the cord with acetone before a 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 didn't 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 [22] 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 hydroxyl groups are 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_4/O_2 plasma treatment [23, 24]. Another approach was to use a vinyl compound in combination with a plasma treatment [25] followed by an RFL dip. Currently the aim is clearly to use only a plasma treatment as a replacement for the RFL technique. Examples are

the application of an atmospheric plasma with a gas mixture of propane, butane and nitrogen [26] or the plasma treatment with an atomized mixture comprised of an polymerizable monomer, a halogenated saturated hydrocarbon and a carrier gas [27]. All these approaches show that plasma treatment has the potential to be a suitable solution for a replacement of the RFL treatment.

COMPARISON

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 requirement and justifies its position on 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 at the production facilities. Disposal of the chemical waste is another major cost factor due to their environmental burden. However, RFL coatings are mainly used further because 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 the RFL ones: 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 precaution 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 wouldn't 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 a very 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 molecules is a direct resolution. 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: The resin-latex coating is missing, which results in a more rapid 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 properties, as they are attached to the main chains of the polymer. This change in cord properties will most likely make adjustments to the material requirements by the manufactures necessary.

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 10 which was observed after an APPJ-treatment (see Figure 8 a). 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 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 11. If the plasma coating reacts with the rubber matrix, the bond is close to a direct bond between cord and rubber. It is to mention, that the plasma treatment only affects the surface which was visible to the plasma. Therefore, an untreated zone inside the cord is established where single filaments of the cord will fail to participate at 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 not entirely adhered 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 tolerable and how this may affect aging behavior.

CONCLUSION

While the classical RFL dip coating is still the industrial standard and delivers sufficient adhesion, its health and environmental burden are increasing the driving force for a replacement. The use of RF-free dips is one step into this direction. However, its advantage is mainly of value for the cord manufacturer, as it reduces health concerns during the dipping process; the chemicals used are still a problem due to toxicity. For the tire companies, a RF-free cord type does not show appreciable advantages in costs,

performance or production performance. A replacement of the RFL cords will only be implemented if the RF-free cords can be used as an one-to-one replacement and if no further changes to the tire construction are necessary.

Plasma treatment is a replacement candidate, because its improved adhesion delivers good properties and it has the potential to simplify the production process. It reduces the health issues during production if less critical chemicals are used. However, most of the chemicals mentioned in literature are not entirely harmless to the environment and therefore no major advantage over the dipping solutions will be achieved. In fact, proper vent and filter systems are mandatory for the exhaust gases. Another fact is that the adhesion interface differs significantly from the nowadays industrial standard as it does not feature a comparable transition zone like RFL. The tire manufacturers may have to make adaptions to their tire constructions in order to apply cords with this type of treatment.

Adding unsaturated bonds to the cord and using them to bind the cord to the rubber matrix is the most consequent approach. It means a significant simplification of the whole production process, and it makes use of additional toxic chemicals obsolete, thus will reduce costs. However, the properties of the adhesion interface will significantly differ as well, not only because of the direct bonding with the rubber matrix, but also because of the possible crosslinking of the unsaturated bonds within the cord itself. Similar to plasma treatment, this technique will require adjustments of the tire design and the building process, as the composite properties have changed. Nevertheless, the advantages of this technology may justify such an effort.

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Table I

Bond energies of common bonding types [2].

Type	Example	E (kJ/mol)
Covalent	C-C	350
Ion-ion	$Na^+...Cl^-$	450
Ion-dipole	$Na^+...CF_3H$	33
Dipole-dipole	$CF_3H...CF_3h$	2
London dispersion	$CF_4...CF_4$	2
Hydrogen bonding	$H_2O...H_2O$	24

Table II

Common 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	-
VP latex (40 %)	212.0	84.8
Water	100.0	-
TOTAL	**500.0**	**100.0**

Table III

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
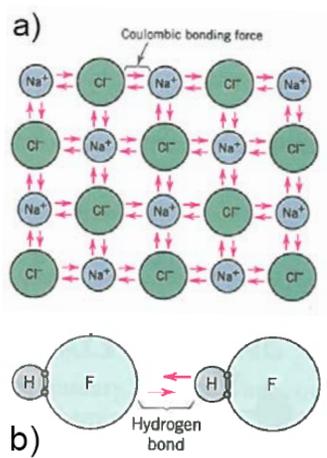
Figure 1: a) Examples for ionic bonding and b) hydrogen bonding [1].
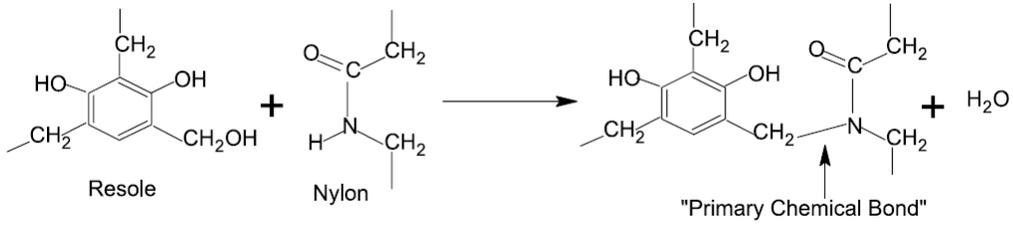
Figure 2: Reaction scheme of a resole and nylon molecule forming a covalent bond [6].

$$R\text{-}\overset{\displaystyle O}{\overset{\displaystyle /\backslash}{CH\text{-}CH_2}} \quad + \quad HO\text{-}\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}\text{-}(PET)_n \quad \rightarrow \quad R\text{-}\overset{\displaystyle OH}{\overset{\displaystyle |}{CH}}\text{-}CH_2\text{-}O\text{-}\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}\text{-}(PET)_n$$

Epoxy   PET end group
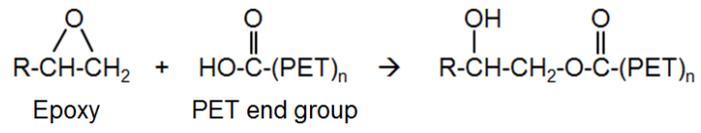
Figure 3: Reaction scheme of an epoxy group with a polyester end group.
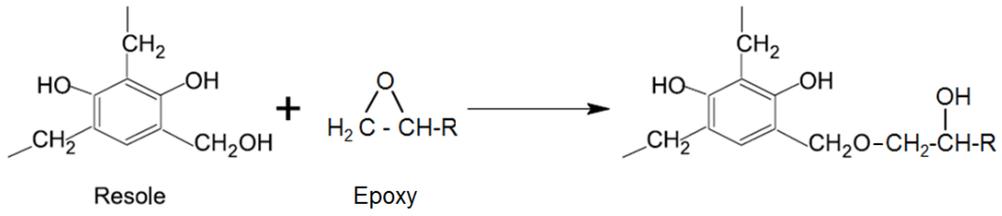
Figure 4: Reaction scheme of sub coating (epoxy) and top coating (resole) [6].
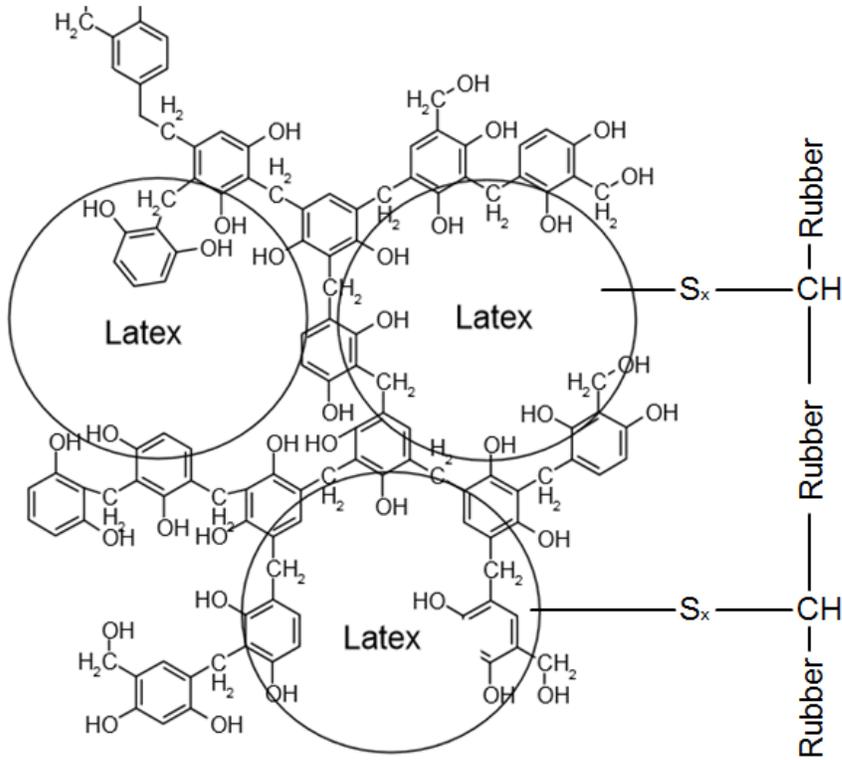
Figure 5: Sulfur crosslinking between the rubber matrix and the latex molecules of the RFL system [7].
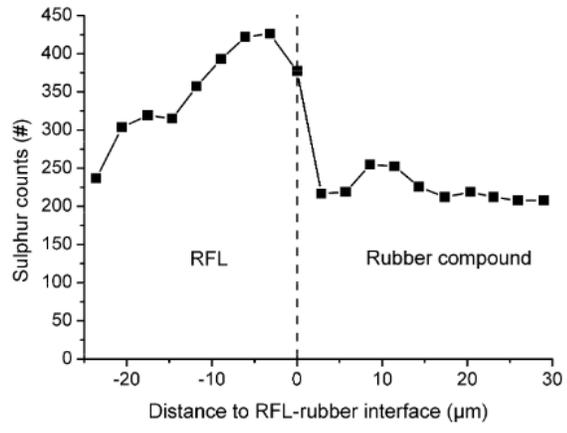
Figure 6: SEM-EDX linescan for sulphur of the RFL-rubber interface [7].
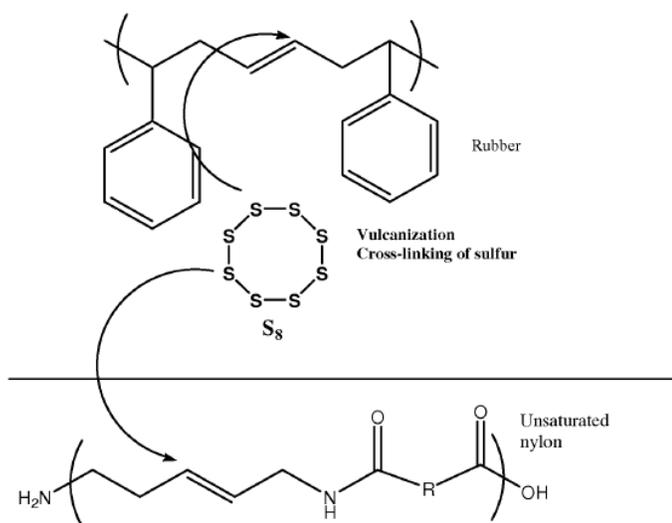
Figure 7: Crosslink reaction between rubber matrix and the innovative unsaturated nylon during vulcanization [10].
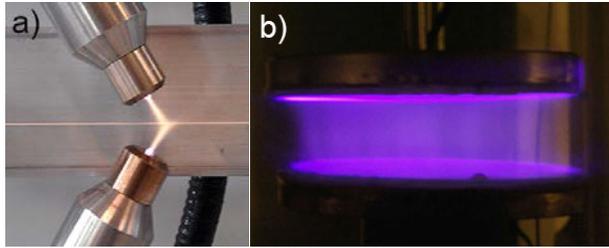
Figure 8: An atmospheric pressure plasma jet (a) and a dielectric barrier discharge [14] (b).
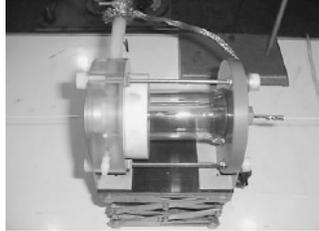
Figure 9: Custom-made plasma reactor with nitrogen atmosphere by Hudec et al [17].
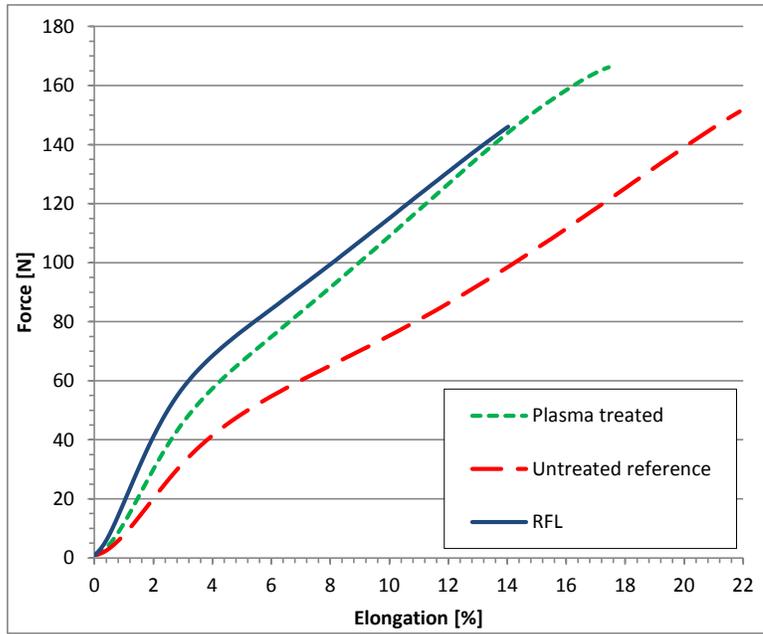
Figure 10: Effect of plasma treatment on Rayon cord in comparison to untreated Rayon cord and RFL dipped Rayon cord.
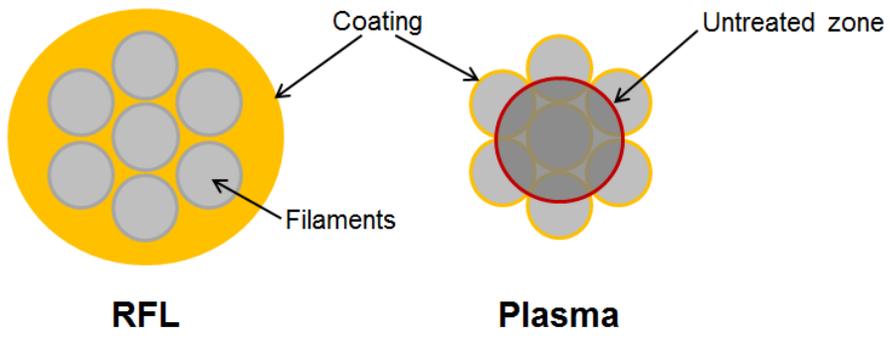
Figure 11: Comparison of RFL dip coating and plasma polymerized coating.

List of figures: