

## **Technologies for Polymeric Cord / Rubber Adhesion in Tire Applications**

A. Louis, J.W.M. Noordermeer, W.K. Dierkes, A. Blume

University of Twente, Dept. of Elastomer Technology and Engineering, P.O. Box 217, 7500 AE Enschede (The Netherlands), a.louis@utwente.nl

### **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.

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 treatment of the polymeric cord is performed in order to enhance the compatibility and form a physical or chemical bond.

### **Industrial Standard Treatment**

The most common technology is RFL, which is the abbreviation for Resorcinol Formaldehyde Latex (RFL) dip that is based on an aqueous 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.

Multiple steps are required for the application of a RFL dip system. 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. 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 [1].

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. 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 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). 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 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.

In general it can be said, that the RFL dip systems still delivers the best results for adhesion promotion between rubber und reinforcing cords compared to alternative systems. That is the main advantage of this treatment, but it also shows some drawbacks, which are the driving forces to substitute the RFL treatment. 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) [2].

### **Alternative Treatments**

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 preferably 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 [1]. The problem thereby is that these measures negatively affect the adhesion strength, which of course is not desired.

Recently, Kordsa Global introduced a RF-free dip solution for nylon cords to the market [3]. 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 [4], 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 to be improved [3].

### 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 [5]. The unsaturated moieties 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 steeper. Clearly, with this approach the amount of chemicals 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 and 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. 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.

Plasma devices are available in several realizations, best known are atmospheric pressure plasma jets (APPJ) or dielectric barrier dischargers (DBD). 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.

Surface activation with plasma is one possibility. The aim is to modify the surface energy of the cord 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 several painting, printing, coating or bonding processes.

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 a 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.

## **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 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 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. 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, an 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. If the plasma coating reacts with the rubber matrix, the bond is rather a direct bond between cord and rubber. It is to mention, that the plasma treatment only affects the surface which is visible to the plasma. Therefore, an untreated zone inside the cord is established where single filaments of the cord will fail to participate at the crosslinking 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.

## References

- [1] R.B. Durairaj, Resorcinol - Chemistry, Technology and Applications (2005), Springer Berlin Heidelberg.
- [2] RAC adopts seventeen scientific opinions, European Chemicals Agency (2012).
- [3] N. Cevahir, A. Sen, European Rubber Journal (2013).
- [4] WO Pat. 091376A1 (2014), Kordsa Global Industry, A.F. Mahallesi, S. Caddesi.
- [5] WO Pat. 020570A2 (2014), Kordsa Global Industry, A.F. Mahallesi, S. Caddesi.