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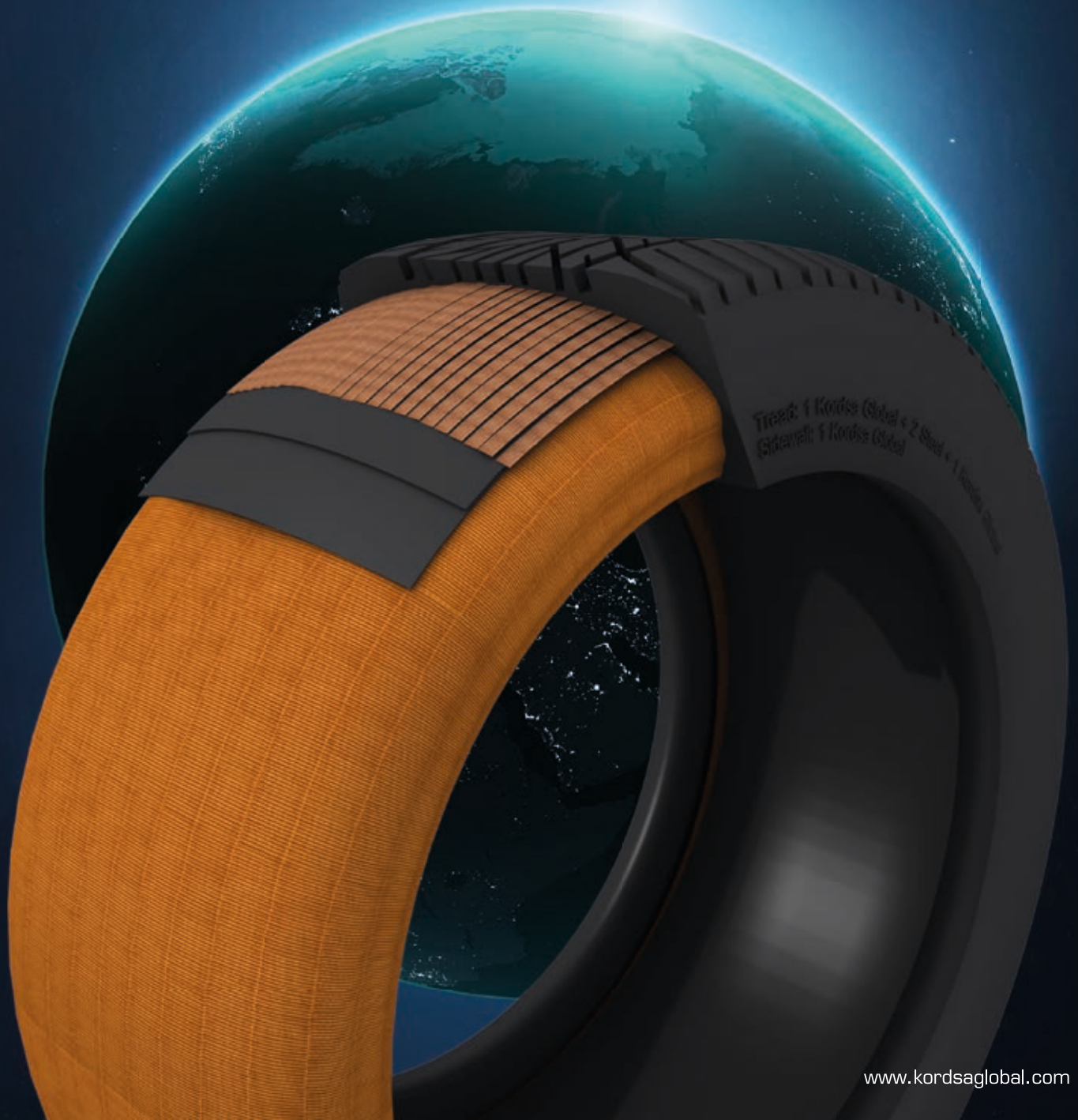
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Resorcinol-formaldehyde-free dip technology for adhesion

By Dr Nurçin Cevahir and Dr Asin Şen

Cord reinforcement of rubber is crucial to many applications, such as high-pressure hoses, transmission belts and conveyor belts. The largest application of cord-rubber composites is the tire. With growing demand for longer-lasting high-performance tires, constant improvement is needed in the performance of reinforcing elements, elastomeric materials and adhesive coating systems.

The main role of the adhesive is to prevent separation at the cord-adhesive and rubber-adhesive interfaces, and within the adhesive itself. This is achieved by employing appropriate cord dipping procedures, which depend on the type of reinforcing elements.

Synthetic fibres are generally difficult to adhere to rubbers, due to differences in polarity and other chemical properties between rubber and fibre. These hinder the formation of a direct bond between the species (ref. 1).

Cord-to-rubber adhesion

The basic requirements for an adhesive to secure satisfactory cord-to-rubber adhesion are as follows (ref. 2):

- Good bonding to both cord and rubber
- Modulus intermediate between those of cord and rubber
- Rapid bond formation
- High fatigue resistance in cured adhesive
- No chemical damage to cord by adhesive
- Compatibility with a range of rubber compounds
- No brittleness or flaking in processing.

Good adhesion between cord and rubber is an absolute prerequisite for satisfactory tire performance. Coating the cords using a resorcinol-formaldehyde latex (RFL) treatment provides sufficient adhesion to rubber compounds. Aqueous RFL dips have the advantage of low viscosity and

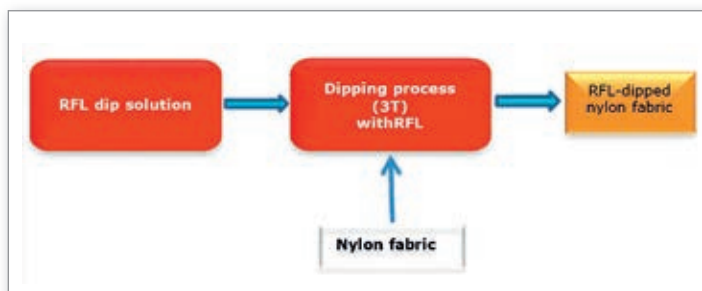


Figure 1 Production of tire cord fabric with RFL adhesive dip solution

thus good wetting-out at the beginning of the curing process. When cured, they become insoluble. The latex imparts the necessary flexibility to the adhesive and reactivity to the rubber, while the resorcinol-formaldehyde formulation provides the required heat and fatigue resistance by forming a three-dimensional matrix (ref. 3).

RFL formulation and hazards

The RFL formulation to be used depends on the type of tire cord; Table 1 shows an example for nylon-66 and Figure 1 outlines the production process.

Among the ingredients of RFL adhesive, formaldehyde is highly toxic to all animals, regardless of mode of intake. Ingestion of as little as 30ml of a solution containing 37 percent formaldehyde has been reported to cause death in an adult human (ref. 5). Formaldehyde is an eye, skin and respiratory tract irritant. Inhaling its vapour can narrow the bronchi, causing fluid to accumulate in the lungs. Aqueous solutions of formaldehyde are very corrosive, and their ingestion can severely injure the gastrointestinal tract, especially the pharynx, oesophagus and stomach (ref. 5).

For these reasons, the acceptable levels of formaldehyde emission from products such as wood panels have been reduced continuously. The driving forces for this reduction have been increased public awareness and hence consumer demand for non-hazardous products, and corresponding government regulation. The recent reclassification of formaldehyde by the Internal Agency for Research on Cancer (IARC) as "carcinogenic to humans" has triggered further concern and responses by trade unions, consumer associations, "green" lobbies, regulatory authorities and the industry itself.

Regulation

Within the EU, formaldehyde is currently classified as a Category 3-R40 substance ("limited evidence of carcinogenic effect"); this is the lowest available EU classification for suspected carcinogens. The classification of formaldehyde in the EU was

reviewed under its REACH (Registration, evaluation, authorisation, and restriction of chemical substances) regulatory regime on chemicals and their safe use. In the United States the current classification by the Environmental Protection Agency (EPA) is that of a "probable human carcinogen" (ref. 6).

REACH came into force on 1 June 2007, and aims to improve the protection of human and environmental health from risks posed by chemicals. Formaldehyde is defined as a "substance of very high concern" (SVHC) in Europe under REACH (ref. 6).

Formaldehyde is an eye, skin and respiratory tract irritant

In principle, REACH applies to all chemical substances; not only those used in industrial processes but also in day-to-day domestic life, for example in cleaning products, paints, as well as materials for goods such as clothes, furniture and electrical appliances. The regime therefore impacts most companies across the EU.

REACH places the burden of proof on companies. To comply with the regime, companies must identify and manage the risks linked to the substances they manufacture and market in the EU. They have to demonstrate to the European Chemicals Agency (ECHA) how the substance can be used safely, and they must communicate risk management measures to users. If risks cannot be managed, authorities can restrict the use of substances in various ways. In the long run, the most hazardous substances should be substituted by less dangerous ones.

Formaldehyde standard 29CFR 1910.1048 of the Occupational Safety & Health Administration (OSHA) and equivalent regulations in states with OSHA-approved national plans protects workers exposed to formaldehyde. It applies to all occupational exposures to formaldehyde

Table 1: Typical RFL formulation for nylon-66 (refs 4,5)

Component	Dry parts per 100 parts of dry latex
Resin solution	
Resorcinol	11
Formaldehyde	6.0
Sodium hydroxide	0.3
Total	17.3
Final RFL dip	
Vinylpyridine latex*	100
Resin solution	17.3
Total solid	20

*A terpolymer of butadiene (70 percent), styrene (15 percent) and vinylpyridine (15 percent)

in liquid and vapour forms, its solutions and materials that release formaldehyde. The permissible exposure limit (PEL) for formaldehyde in the workplace is 0.75 parts per million of air (0.75 ppm) measured as an eight hour time-weighted average (TWA) (ref. 7). The standard includes a second PEL in the form of short-term exposure limit (STEL) of 2 ppm, which is the maximum exposure allowed during a 15 minute period.

RF-free dip solution
prioritised to meet future
regulatory requirements

Despite increasing environmental and safety concerns, no other adhesive system had so far been developed as an alternative to resorcinol-formaldehyde-based adhesives, which have been widely applied since 1935. Even though all necessary precautions against formaldehyde emission have been taken at Kordsa Global sites so far, developing an RF-free adhesive dip solution was prioritised with a view to meeting future regulatory requirements. The company's new adhesive system performs better than an RFL dip.

Preparation of RF-free dip solution

The RF-free dip solution is prepared by mixing resin and latex solutions. Cord fabric is passed through the RF-free dip solution and then heat-treated in drying and curing ovens. Residence time, temperatures and tension are optimised to obtain the desired strength and adhesion properties.

RF-free dipped fabric is whitish in colour, whereas RFL-dipped fabric is brown (Figure 3).

Nylon cords and fabrics treated with



Figure 4 RF-free (left) and RFL treated cords (right) after vulcanisation in rubber compounds

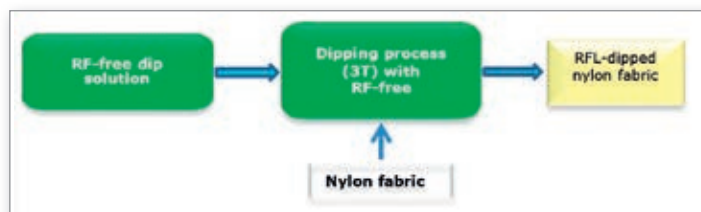


Figure 2 Production of tire cord fabric with RF-free adhesive dip solution



Figure 3 Tire cord fabric dipped with RF-free (left) and RFL solutions

RF-free adhesive were embedded in an uncured rubber compound which was then cured for adhesion testing. Static adhesion tests were based on the standards ASTM D4776 (H-adhesion), ASTM D4393 (peel adhesion) and CRA-ST (according to a method provided by the customer). The cord appearances after the adhesion tests are shown in Figure 4. A dynamic adhesion test according to the ASTM D430 protocol provided information on the fatigue life of the cord-rubber composite under cyclic strain.

The required adhesion was obtained with a lower dip pick-up (DPU) when an RF-free dip was used. DPU values for nylon fabrics were determined as 3.0-3.5 percent.

The advantages of RF-free dip solution over RFL dip solution are as follows:

- Resorcinol and formaldehyde use are completely eliminated
- Formaldehyde emission is eliminated
- RF-free dip is compatible with REACH regulations
- Desired adhesion is achieved with lower DPU
- Fatigue adhesion performance is improved.

The mechanical properties of RF-free-dipped nylon-66 fabrics were either superior or comparable to those of RFL-dipped fabrics. Figure 5 shows that initial adhesion was 5-7 percent higher, and up to 10-15 percent more fatigue adhesion retention was attainable with RF-free dip-treated fabrics.

Performance testing of tires made with RF-free dipped fabrics is in progress. RF-free dip adhesive formulations for PET cords are also under investigation. The principal aim is to eliminate the pre-dip activation step for PET fabrics and use only one type of RF-free adhesive solution for all types of tire cord fabric.

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- Drs Cevahir and Şen are with Kordsa Global.

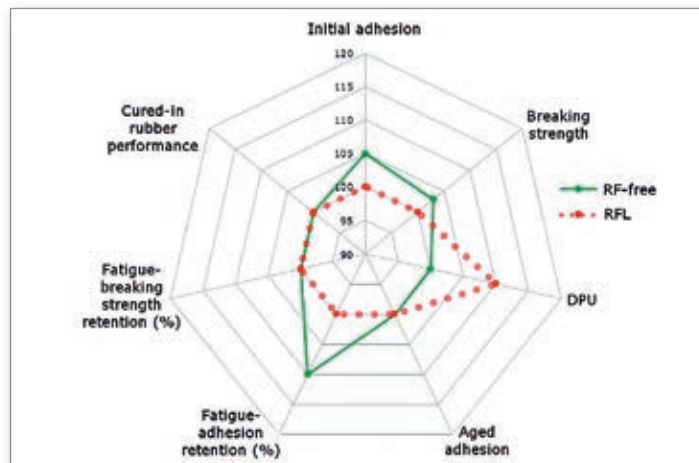


Figure 5 Comparison of properties of RF-free and RFL-dipped fabrics