Rubber Products
WHITE PAPER

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From raw materials to tailor-made applications: How to develop rubber products?

Abstract: Each rubber product consists of a certain elastic material, designed in a specific shape, sometimes coated with a tailored coating and should fulfill on or more functions in a certain application. The rubber material and product geometry influence both production process and product functionality as well as the other way around. This white paper describes how each rubber compound is uniquely defined by its ingredients as well as by the mixing process. Furthermore, an overview is given on various techniques to analyze rubber materials and final rubber-containing products such as wiper blades. Finally, it is explained how rubber products and processes can be optimized by means of Design of Experiments (DOE) methodology and finite element simulations.

1. Introduction

Rubbers are elastic materials, made from long-chain molecules (called polymers) which are cross-linked together in a vulcanization process. The alternative name for a rubber is “elastomer”. The term rubber is used 3-fold: to name the base polymer responsible for the major characteristics of the final product, the semi-product which consists of the raw polymer mixed with additives to enhance particular properties and it also refers to the final product which is already shaped and cured.

Due to their elastic nature, rubbers are very flexible materials (E modulus 1-100 MPa) with glass transition temperatures well below 0 °C. Furthermore, they can be stretched repeatedly to large levels of deformation (elongation at break 100-1000%) and upon releasing of the applied stress, immediately return to their initial shape. Due to this unique behavior and due to a number of other interesting material properties, rubber is used for a huge amount of static as well as dynamic applications.

- **High elasticity:** belts, elastic rubber bands, membranes for loud speakers
- **Sealing:** canvas cover, protective clothing, gloves, hoses, gaskets, joints, windshield wipers, membranes
- **Biocompatibility:** food industry: seals, spatula, baby nipple, medical industry: tourniquet, catheter, prostheses, implants, bandages
- **Damping:** Mattresses, foams, anti-vibration dampers for buildings, bridges, train rails, shock absorbers
- **Adherence & High friction:** tires, conveyor belts, running-tracks, skate board wheels, shoe soles
- **Adhesion:** Glue
- **Thermal & electrical insulation:** cable covering
- **Low gas permeability:** Inner-liner of tires, air chambers, balloons, septa for drug containers

Each rubber product is made from a certain rubber compound, and shaped in a certain form. In some cases, an additional coating is used to give the product certain surface characteristics. The final rubber product should fulfill one or more functions in a certain application.
Both rubber material and product shape influence the final product functionality as well as the selected rubber production process. At the same time the product function and the production process influence the degrees of freedom regarding material selection and product geometry (see Figure 1).

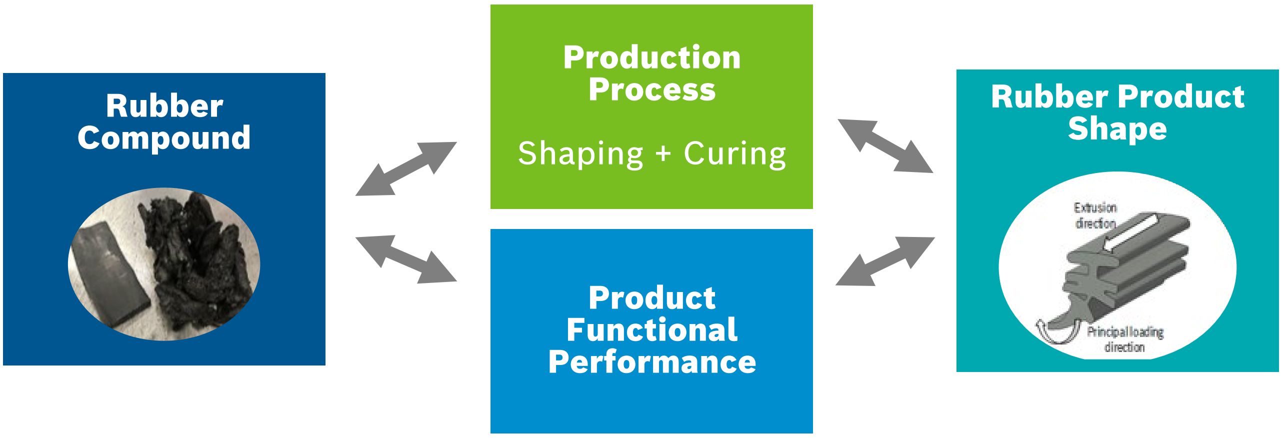

Figure 1.

The rubber compound is determined by the rubber recipe as well as by the rubber mixing process. Both the type and amount of different ingredients in the mix, as well as how they are mixed with each other defines the final rubber compound properties.

Ingredients of a rubber recipe:

Polymers: About 50-60% of the rubber compound consist of one or more basic elastomers, which define the major characteristics of the final compound. Besides NR, which comes from a natural source (rubber trees), most elastomers are synthetic products. A huge amount of elastomer types are available on the market. Figure 2 displays the main elastomer types used for wiper rubber manufacturing.

Fillers: In order to give the compound static as well as dynamic mechanical strength and durability, fillers are added to the rubber matrix. They can be classified into reinforcing fillers (high activity carbon blacks), semi-reinforcing fillers (lower activity carbon blacks and silica) and non-reinforcing fillers (white fillers such as calcium carbonate, chalk, clays,...). The reinforcing potential of a filler such as carbon black is determined by its surface area (the smaller the dimension of the primary particle, the higher the surface area) and by its surface structure (the more irregular the shape of the carbon black aggregates, the higher the structure).

Plasticizers: Mineral oils (parrafinic, napthenic and aromatic oils) or synthetic molecules (mainly aliphatic ester-types) are used as plasticizers. Polarity of the plasticizer should be similar to the polarity of the used elastomer in order to be effective. Plasticizers are added to improve the dispersion of fillers in the rubber matrix during mixing (especially required when high filler loadings are used), enhance flow during processing of the rubber by lowering the viscosity, improve the cold flexibility of the rubber compound by lowering the glass transition of the matrix and have an influence on the final physical properties of the rubber compound since they stay embedded in the rubber matrix.

Vulcanisation chemicals (curatives): Vulcanising agents create crosslinks between the rubber polymer chains, thereby forming the cured elastomer network. These vulcanization chemicals are usually sulfur or peroxide based. Sometimes also other special curing agents are used. The course of the vulcanization reaction influences the final physical properties such as tensile strength, elongation at break etc.

Accelerators: They increase the crosslinking reaction speed and thereby allow to use lower amounts of sulfur curing agent for optimal curing performance.

Activators: They activate the vulcanization process and improve the efficiency of accelerators in the system. Examples are stearic acid and zinc oxide.

Retarders: Sometimes the vulcanization reaction has to be slowed down to a controlled rate. This can be achieved by adding retarder molecules.

Process aids: Molecules that help the rubber compound to be processed, for instance during mixing, milling, straining, extrusion or injection molding processes. For instance lubricants, anti-sticking agents, etc.

Protecting agents: In order to protect the rubber compound from oxygen attack, anti-oxidants are added which prevents double bonds inside the rubber elastomer from being changed. Anti-ozonants are added to prevent damage from ozone molecules, generated under UV-light. Finally, also metal-deactivators and flame retardants can be added.

Other ingredients: color pigments, blowing agents, bonding agents, tackifiers can be part of a rubber compound, depending on the target application

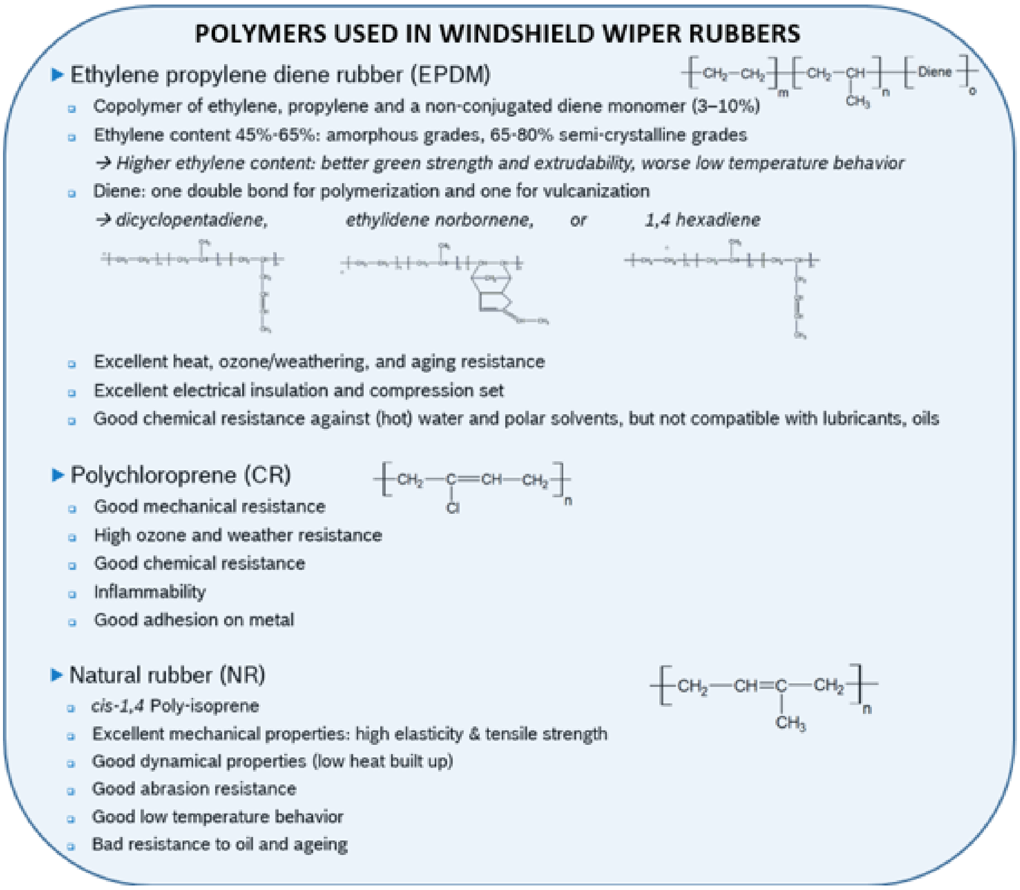

Figure 2.

Mixing of rubber compounds:

Mixing of the rubber ingredients can be done in basically 2 ways.

The first method uses an open mill whereby the ingredients are step-by-step added on top of the mill. The mill consists of 2 counter-rotating rolls which can be cooled or heated as needed. The rubber ingredients are mixed by the shear forces that take place at the “nip” between the rolls. When the mixing is finished, the final compound is removed from the mill as sheets or strips.

The second method uses an internal mixer that consists of 2 counter-rotating rotors in a large housing. Rubber ingredients are added in dedicated order into the shaft of the mixer and pressed down onto the rubber rotors by means of a pressurized ram. The 2 most used types of rotor types are tangential rotors or intermeshing rotors. The rubber is mixed by the shear between the rotors and the housing, and all equipment is cooled in order to avoid overheating of the compound.

The mixing process is essential to achieve good compound properties since it ensures that the reinforcing fillers are well-mixed in. The reinforcing potential of a carbon black filler can only be reached when the contact area between polymer and carbon black is optimal. When carbon black is added to the polymer in the mixer, first an incorporation of the carbon black big agglomerates into smaller agglomerates takes place. Secondly, the small agglomerates are further broken down into carbon black aggregates, this phase is called dispersive mixing.

Finally, distributive mixing takes place whereby the coherent aggregates are separated into smaller aggregates and primary particles. The final rubber matrix can be characterized concerning macro- and micro-dispersion which influence the rubber-filler interactions and the filler-filler interactions. These interactions build the final reinforcing properties of the rubber compound.

2. Rubber material and product performance: Relation of functional performance and process-ability to physical properties

Rubber materials can be analyzed in various ways. Although the following list is by no means exhaustive, it gives a good overview of different analysis tests that can be performed on rubber samples.

Chemical analysis by means of for instance Differential Scanning Calorimetry (DSC) (DIN 53765), Thermo-Gravimetric analysis (TGA) (NF T46-047), density (ISO 2781, ISO 1183) or extraction of volatile components. These techniques give insight on the rubber composition which can be useful for analysis of unknown rubber samples. Also, the resistance of the rubber against different solvents can be investigated by swelling tests (DIN ISO 1817). If the rubber is resistant against the tested fluid, it will no swelling after being immersed in the liquid for a certain time and temperature applied.

Rheological analysis of uncured rubber compounds:

- Moving Die Rheometer (MDR) is used for characterization of rubber curing. The uncured rubber sample is pressed between 2 heated plates which are oscillated and the change in torque due to curing is measured. (ISO 6502 / DIN 53529 / ASTM D5289).
- Mooney Viscometer is used to determine the Mooney viscosity of the uncured compound and can also give information on the tendency of a compound to resist premature curing (called scorching) at a certain process temperature. (ISO 289 / DIN 53525 / ASTM D1646).
- Rubber Process Analyzer (RPA) is used for investigation of the process-ability of a compound. It can for instance determine the torque and resulting shear modulus and viscosity of an uncured rubber at different frequencies, or strain amplitudes. Hereby can be simulated how a rubber reinforcing network is influenced by processing shear such as happening during mixing or extrusion. (ASTM D5289, D6048, D6204, D6601, D7050, D7605 / ISO 6502, 13145 / DIN 53529).

(Dynamic) Mechanical analysis of cured rubber products:

- Hardness measurements: Shore hardness on molded plates or micro-hardness on final rubber product geometries. (DIN ISO 7619, DIN EN ISO 868, DIN 53505, DIN ISO 48).
- Tensile or compression tests gives information on the force needed to deform the rubber. A tensile tester measures a stress-strain curve for a rubber dumbbell sample which is elongated in tensile mode until breakage of the sample resulting in core parameters such as modulus at 100% elongation (mod100), tensile strength and % elongation at break. In a compression test, the rubber is compressed and the force required to do so is measured. (DIN 53504, ISO 37, ASTM D575)

- Rebound elasticity measures the ratio between the amount of energy recovered (elasticity) and the amount of energy dissipated by allowing a pendulum to impact on the rubber sample and measuring the rebound of this pendulum. (DIN 53512, ISO 4662).
- Dynamic mechanical analysis (DMA): a rubber sample is subjected to a static strain on which an additional dynamic sinusoidal strain is superimposed. The reaction of the rubber to this dynamic strain is measured. Typical methods are frequency-sweeps, temperature-sweeps, strain sweeps and hysteresis measurements. (DIN EN ISO 6721-1)

Ageing and durability tests of cured rubber products:

- Tear strength or tear propagation strength measures the resistance for a rubber sample towards cracking or tearing. (ISO 34, ASTM D624).
- Tension set measures the residual elongation of a rubber sample after being elongated for a certain percentage (for instance 25%) for a certain time at a certain temperature. It is a measure for the heat ageing resistance of the rubber product. (DIN ISO 2285, ISO 188). Similarly, compression set measures the residual compression of a sample (ASTM D395).
- Abrasion test measures the rubbers resistance against abrasive wear caused by rubbing it with a sand-paper of a certain grain size using a rotating cylindrical drum device. (ISO 4649).
- UV light and weather resistance: after subjection to a certain period of UV light and or moisture, the physical properties of the rubber or any discoloration is tested. (ISO 4892-2)
- Ozone resistance: The rubber sample is stretched to certain elongation and subjected to ozone. The resistance to cracks is measured. (DIN ISO 1431-1)

Off-course not only the analysis of the rubber material itself is important, the final product in which the rubber material is used should also fulfill its application under various conditions. The primary function of a wiper blade is to act as a dynamic sealing between the rubber-glass contact, lubricated with water. Wiper blades undergo various tests to investigate their performance on vehicles such as:

- wipe quality in new condition
- durability (wipe quality after for instance 200,000 cycles)
- window of operation (force and angle range in which the wiper blade performs optimal)
- heat and cold ageing (performance of the wiper blade after several hundred hours of storage in for instance 80°C or -10°C)
- resistance to wear: adhesive wear due to rubber-glass friction, abrasive wear to to presence of sand, dust, or bugs on the windshield
- Noise tests: During operation, wipers can generate a number of running noises (humming, squeak, smacking, sandy noises, etc.) and reversal noise (when the wiper blade changes direction). Among others, noises are influenced by the windshield conditions (hydrophilic, hydrophobic, wet, dry, damp-dry, etc.)

On-vehicle testing is time-consuming and expensive. Therefore, the aim is to find correlations between the material tests described above and vehicle tests. When a lab-test can predict the functional behavior of the final application, it is faster and cheaper to optimize the rubber product by means of these material tests.
Secondly, process-ability tests of rubber materials on serial production equipment such as extrusion lines or injection molding infrastructure is also expensive. Again, if such large-scale tests can be avoided or only performed on optimal compounds, this saves a lot of time and money. So also correlations are determined between process-ability of a rubber mixture and the above mentioned material tests.

3. Optimization of rubber products and processes by DOE approach or FE simulations

As mentioned early in the document, the rubber material and product geometry influence the production process and product functionality and vice-versa. In order to optimize the rubber material, geometry, production processes or functionality a lot of requirements need to be met at the same time. Therefore, optimization by means of a one-factor-at-time (OFAT) approach is insufficient and unsatisfactory.

The OFAT approach is time and labour consuming, and very often the most optimal material, shape, process settings or product functionality is even not found due to the complexity of the investigation. A much better and efficient methodology is to make use of design-of-experiment (DOE) approach (for an example see Figure 3). With DOE, a number of input variables (also called input factors) are selected which are deliberately varied between certain borders. Up to 6 different variables can easily be selected and simultaneously varied. By means of statistical DOE software, a test-plan with a limited number of experiments is generated. All tests are carried out and a number of output responses (for instance the above described material tests) are measured and entered into the DOE software.

Input Factors	Low Value	High Value
Polymer A	0	100
Polymer B	0	100
Filler	50	120
Plasticizer	20	50
Process Aid	0	10
Cross-Linker	2	6

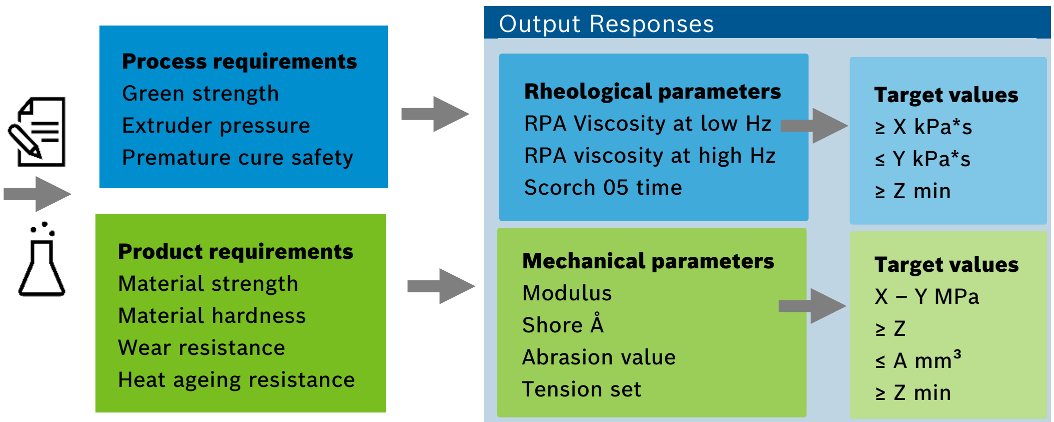

Figure 3.

The software performs a statistical analysis of the data. For each output response, it is calculated which input factors are most significant. The model describes the relation between input and output as an equation containing first order, second order and interaction parameters. The relations can be visualized in the prediction profiler of the DOE model (see Figure 4).

Some relations are linear, while others are non-linear. The prediction profiler can now be used to simulate the output responses for a certain set of input factors (in this example compound ingredients). This method allows to find the best ingredient combination to result in the most optimal combination of output responses.

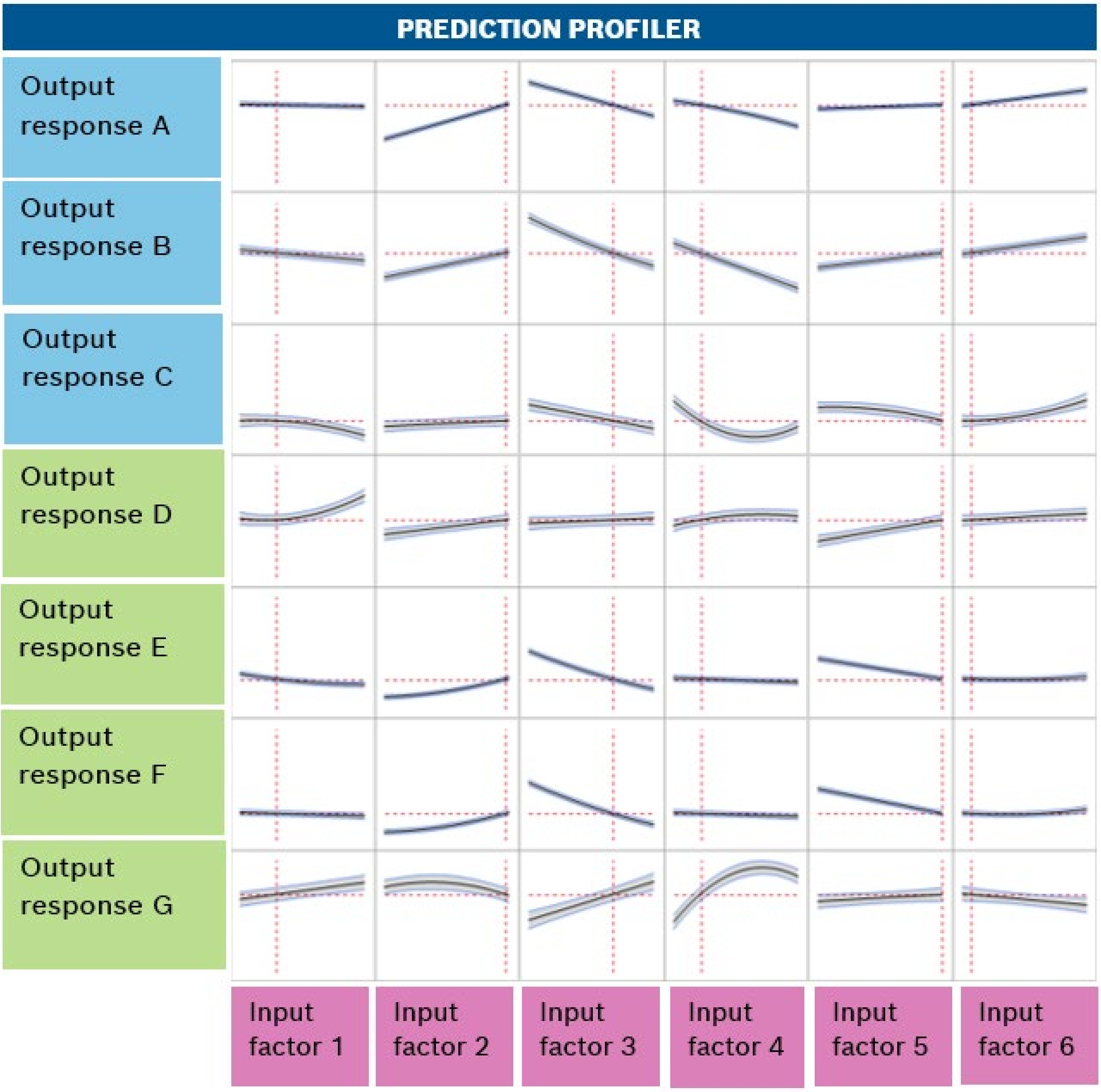

Figure 4.

Finally, rubber products can also be optimized by means of Finite Element (FE) analysis. This technique is mainly used to optimize rubber profile geometries, but can also be used for other purposes. It can simulate for instance how and where strain and deformation are occurring in a rubber product (consisting of a certain material and shape) when application-related stresses are applied.

Based on this information, rubber product materials and geometries can be optimized in order to better fulfill the target application, to enhance the products life-time or to reduce undesired side-effects such as noise generation, internal heating or structural damage.

4. Company profile and rubber expertise

The Bosch Group was set up in Stuttgart in 1886 by Robert Bosch (1861–1942) as “Workshop for Precision Mechanics and Electrical Engineering”. Nowadays it is a leading global supplier of technology and services. It employs roughly 400,000 associates worldwide. Its operations are divided into four business sectors: Mobility Solutions, Industrial Technology, Consumer Goods and Energy and Building Technology. The company generated sales of 78.0 billion euros in 2017 from which 60,5% (€47.4 billon) came from the Mobility Solutions business area.

Bosch improves quality of life worldwide with products and services that are innovative. The basis for the company’s future growth is its innovative strength. At nearly 130 locations across the globe, Bosch employs some 68,700 associates in research and development.

As part of the mobility solutions business area and integrated in the Electrical Drives division Robert Bosch Produktie N.V (RBBE) is a world leader in the development and manufacturing of wiper blades and wiper arms. As a Bosch Group leading plant it also supports production sites in Asia, Europe and South America. Located in Tienen (Belgium) the factory was founded in 1973 and currently gathers around 900 employees. With a turnover of €151 million in 2017 RBBE manufactured 39 million wiper blades, 12 million wiper arms and 0,8 million wiper rubber/refill for both aftermarket and original equipment.

At RBBE, all core competencies are in house for development and manufacturing of high quality rubber products.

- Product development:
    - Rubber compounding
    - Profile geometry design
    - Coating development
    - FE simulations
- Process development:
    - Rubber production processes
    - Coating application processes
    - Rubber analysis method development
- Production:
    - Rubber mixing and milling
    - Extrusion
    - Injection molding
    - Vulcanization (salt bath)
- Laboratory:
    - Lab-scale mixer, mill, pressing, extrusion
    - Rheological analysis
    - (Dynamic) mechanical analysis
    - Surface characterization
    - Chemical analysis
- Testing:
    - Probe testing (wear, friction,...)
    - Wiper blade testing on vehicle

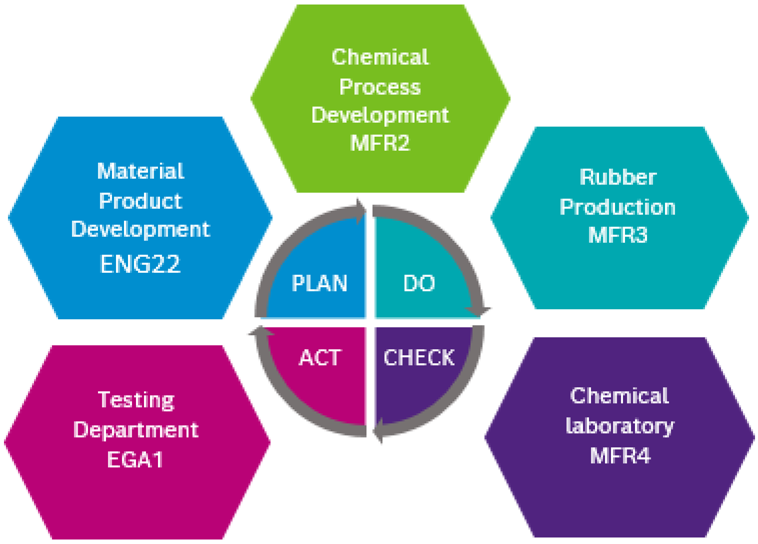
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Figure 5.