



Fraunhofer

Better than natural rubber

BISYKA

BIOMIMETIC SYNTHETIC RUBBER

FRAUNHOFER
EXPERTISE

Elastomers
Life sciences
Silica fillers
Scale up



30% less
abrasion

Superior
roll resistance

Can be
produced
in **existing**
plants

THE FRAUNHOFER-GESELLSCHAFT

ABOUT THE FRAUNHOFER-GESELLSCHAFT

The Fraunhofer-Gesellschaft is Europe's leading organization in applied research. It is made up of 72 institutes and research facilities located throughout Germany. More than 26,600 employees generate an annual research volume of more than 2.5 billion euros. Of this, more than 2.1 billion euros come from

contract research, 70 percent of which is through contracts with industry and with publicly financed research projects. International collaboration with outstanding research partners and innovative companies worldwide provides direct access to major scientific and economic regions now and into the future.

On behalf of the Fraunhofer-Gesellschaft,
I would like to congratulate the BISOYKA consortium on its excellent outcomes in the field of biomimetic synthetic rubber.

Within the framework of MAVO, Fraunhofer's internal research program for market-oriented preliminary research, the Fraunhofer-Gesellschaft bundles the expertise of various institutes into original preliminary research projects.

BISOYKA is an excellent example of how synergies can be used effectively in this way to develop new and original solutions.



Dr. Lilja Meißner

Fraunhofer-Gesellschaft
Internal Research Program

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WHY IS RUBBER SO IMPORTANT FOR THE AUTOMOTIVE INDUSTRY?

Fraunhofer's project on biomimetic synthetic rubber "BISYKA"

Natural and synthetic rubber are an integral part of more than 40,000 everyday products. They have become an essential material for tires. With a production volume of almost thirty million metric tons per year, rubber is one of the world's most important strategic raw materials. Natural rubber makes up nearly 50 percent of global rubber production. The remainder is synthetic rubber.

Both types of rubber have their advantages: Natural rubber has unique mechanical properties while its synthetic counterpart is characterized by very high chemical uniformity, batch homogeneity and good processability. However, synthetic rubber does not achieve the outstanding mechanical performance of natural rubber. Natural rubber is therefore crucial for many applications. However, it is becoming increasingly difficult to meet the demand for it.

Natural rubber is an important raw material for truck tire treads.

Natural rubber

Around 99 percent of natural rubber is produced from the latex of the rubber tree (*Hevea brasiliensis*). The rubber tree previously only grew in the tropical Amazon Basin. Today,

Thailand, Indonesia and Malaysia are its three largest producing countries. However, the climatic conditions required by the rubber tree severely limit the area in which it can be cultivated. This makes an increase the amount of natural rubber nearly impossible. In addition, rubber latex only contains 25 to 35 percent rubber and cannot be harvested until after an initial growth phase of around seven years. Things are made even more difficult by the fact that the population of Brazilian rubber trees is currently under severe threat by South American leaf blight. A spread to the cultivation regions in the Indian Ocean cannot be ruled out.

These issues along with additional shortages caused by weather-related crop losses, a trend towards price-fixing in the producing countries and a general increase in demand mean that potential substitutes for natural rubber are increasingly being sought worldwide. Dandelion rubber offers one such alternative. Its raw material and material properties are almost identical to those of the rubber tree. However, its advantage comes from its significantly shorter harvest and regeneration cycles as well as its lower demands on soil quality and climate.

Biomimetic synthetic rubber "BISYKA"

Producing synthetic rubber with the same mechanical properties as natural rubber is particularly interesting from an economic perspective. The advantage here is that we are able to fall back on existing synthesis technologies and production



Figure 1 Rubber is essential for tire applications.

capacities. It is relatively easy to produce the relevant quantities and is a reliable way to expand the raw material base, thereby ensuring that (electro)mobility can increase worldwide.

Five Fraunhofer Institutes therefore set themselves the task of researching the origins of the unique mechanical properties of natural rubber and transferring these to synthetic rubber – with success. The biomimetic synthetic rubber, or “BISYKA” for short, is an innovative material with high value-adding potential.

The project received funding for three years through MAVO, an internal program of the Fraunhofer-Gesellschaft for market-oriented preliminary research. |

Fungal infestation of rubber trees threatens worldwide production of rubber.

Why was the BISYKA project launched in 2014?



Research has sought to replicate the properties of natural rubber ever since the beginning of synthetic rubber production.

The outstanding properties of natural rubber are most probably due to the exceptional purity of its microstructure in combination with specific biocomponents. Today, we polymer chemists have nearly perfected the high structural purity of its “sister system” polybutadiene. Thanks to new developments in the field of transition metal catalysts, used in the coordinative polymerization of dienes, the number of imperfections is now close to zero.

As far as the influence of biocomponents is concerned, we have learned a lot from our colleagues at the Fraunhofer IME and their successful work on dandelion rubber. They have gained a great deal of insight into the type of biocomponents, their etiology and their effect on the biosynthesis of polyisoprene. Fraunhofer has now obtained all the necessary competencies along the elastomer value chain – from polymer synthesis and composite production, including fillers, to analytical expertise.

The time was simply ripe for a new attempt in 2014!

Dr. Ulrich Wendler
Fraunhofer IAP

WHAT MAKES NATURAL RUBBER SO UNIQUE?



Composite materials made from natural rubber are indispensable for many applications that require components with a high mechanical strength, e. g. for truck tire treads or conveyor equipment. Their high tear resistance and good abrasion resistance make them unique.

Despite intensive efforts, scientists had been unable until recently to synthetically reproduce rubber with a property profile corresponding to that of natural rubber. For example, the mechanical properties of synthetic polyisoprene, such as modulus of elasticity, tensile strength and tear strength, have been inferior to those of natural rubber. Among other things, this is attributed to the extremely high uniformity of the molecular architecture – the arrangement of the double bonds – which is typical for such biological polymers.

Synthetic rubber has so far failed to match natural rubber in terms of abrasion resistance.

Strain-induced crystallization

Strain-induced crystallization is what gives natural rubber its advantageous mechanical properties. It is typically found to have deformation amplitudes of 300 to 400 percent¹. Researchers have been aware of this phenomenon for a long time and various methods can be used to detect it, such as wide-angle X-ray scattering or calorimetry. The fact that high strain occurs locally in nanoparticle-filled composites and at the tip of propagating cracks is evidence that crystallization induced in this way improves the mechanical properties of natural rubber-based materials².



Natural rubber makes up nearly 50 percent of global rubber production. The remainder is synthetic rubber.

However, the effects caused by strain-induced crystallization are observed to a significantly lesser degree in synthetically produced polyisoprene-based systems³. This is caused by the 100 percent cis-1,4 content of polyisoprene chains in natural rubber as well as the endogenous biocomponents contained within it, i. e. proteins, phospholipids, terpenes and fatty acids.

Additional influence of biocomponents

Both its biocomponents and its high microstructure purity are crucial for the outstanding mechanical properties and the strain-induced crystallization of natural rubber. Increasing strain-induced crystallization in cis-1,4-polyisoprene that has a high microstructure purity and few impurities seems logical, since defects along the polymer chain prevent the formation of relatively thick crystallites (lamella thickness >10 nm) in highly oriented shish kebab-like structures, as observed with strain-induced crystallization.

However, comparative investigations of natural rubbers, whose biocomponents were extracted, and synthetic polyisoprene systems reveal that the perfect microstructure of the polyisoprene chains is not the only reason for the advantageous mechanical properties of natural rubber. There are clear indications that the very low percentage of biocomponents (in the single digits) contained in natural rubber foster strain-induced crystallization and thus improve its mechanical properties.

So far, only assumptions can be made about the underlying mechanism: Either the bioadditives act as nucleating components capable of crystallization or they support or accelerate the formation of pre-oriented sequences in the polyisoprene chains, which in turn are important for strain-induced crystallization. |

High microstructure purity and biocomponents are behind the outstanding mechanical properties and the strain-induced crystallization of natural rubber.

UNDERSTANDING DANDELION RUBBER

Natural components make innovative elastomers

Natural rubber – a unique plant-based biopolymer

Although ~1800 plants synthesize natural rubber, a widely used biopolymer with applications ranging from medical devices to vehicle tires, only a few species produce rubber molecules with a sufficient molecular mass of more than 1,000,000 g/mol. The Russian dandelion *Taraxacum koksaghyz* is one such species. It is also faster growing and more sustainable than the rubber tree *Hevea brasiliensis*, from which most natural rubber is currently obtained (Figure 1).

Natural rubber is mostly (93–95 percent) composed of the polymer poly(*cis*-1,4-isoprene) with the remaining 5–7 percent made up of primarily species-dependent low-molecular-weight compounds and proteins. These are generally part of the rubber biosynthesis machinery and remain attached to the rubber following isolation. Due to the high molecular mass of poly(*cis*-1,4-isoprene), it must be stored by the plant within

special membrane-enclosed vesicles known as rubber particles, which are also the sites of rubber biosynthesis (Figure 2).

Rubber particles only form in specialized plant cells that have unique morphological and physiological features to support rubber biosynthesis, including a rich supply of cellular energy, isoprene monomers, enzymes for polymer biosynthesis, emulsifiers in the form of low-molecular-weight compounds, and proteins that prevent polymer agglomeration.

In recent years, Fraunhofer IME researchers have investigated the Russian dandelion and identified the various factors involved in poly(*cis*-1,4-isoprene) synthesis, gaining deep insight into the underlying physiological mechanisms. A process has also been developed to isolate natural rubber from dandelion tissues. Thanks to this research, the Russian dandelion is now regarded as the most promising natural rubber producer for

COMPETENCIES

The Fraunhofer IME

The Fraunhofer Institute for Molecular Biology and Applied Economy IME conducts research in the applied life sciences from the molecule to the ecosystem. The institute's interdisciplinary organization and its laboratories with state-of-the-art equipment enable a broad range of research and services in the fields of Molecular Biotechnology, Applied Ecology and Bioresources, and Translational Medicine. This breadth of scientific and methodological expertise is the strongpoint of the Fraunhofer IME. It enables the development of innovative and holistic solutions for the great challenges facing our society in areas such as the bioeconomy, sustainable agriculture and health research.

The research division Plant Biopolymers in Münster develops novel concepts for the optimized use of biomass and plant-derived molecules by applying biotechnology and advanced breeding methods. Research focuses on biopolymers such as starch, inulin, proteins and natural rubber, but also includes the use of biotechnology to produce secondary metabolites for applications in human and veterinary medicine. Excellent national and international ties to partners from science and industry ensure that recent findings and current needs are directly incorporated into ongoing areas of research.



Figure 1
Greenhouse-cultivated
Russian dandelion.

temperate climates. This has enabled the production of a wide range of product prototypes, which have confirmed that dandelion rubber has mechanical and physicochemical properties equivalent to Hevea rubber. As well as direct product applications, the Russian dandelion has also been used to study the origin and composition of natural rubber in detail. This allowed links to be made between the individual components of rubber and its mechanical properties. It is at this point that the Fraunhofer IME became involved in the MAVO BISYKA project.

Isolating and characterizing the components of natural dandelion rubber

As part of MAVO BISYKA project, the Fraunhofer IME has been able to isolate, characterize and manufacture the components of natural dandelion rubber that confer its physicochemical characteristics. This was achieved by isolating

dandelion rubber and using various solvents to separate it into hydrophilic and hydrophobic substance classes.

The individual lipids and proteins were also extracted from these separate phases for further characterization (Figure 3). The lipids included various triterpenes/triterpenoids and phospholipids, each of which could have an emulsifying effect on the rubber particles and the polymer contained within them. The proteins in natural rubber interact with the components of cell membranes (such as phospholipids) to stabilize the rubber particles. The specific lipid content as well as the proteins and their degradation products may explain why synthetic and natural isoprene rubber have different properties. The analysis of natural rubber samples from which these components had been extracted showed significantly reduced strain crystallization. The influence of triterpenes/triterpenoids on strain crystallization was found to be >

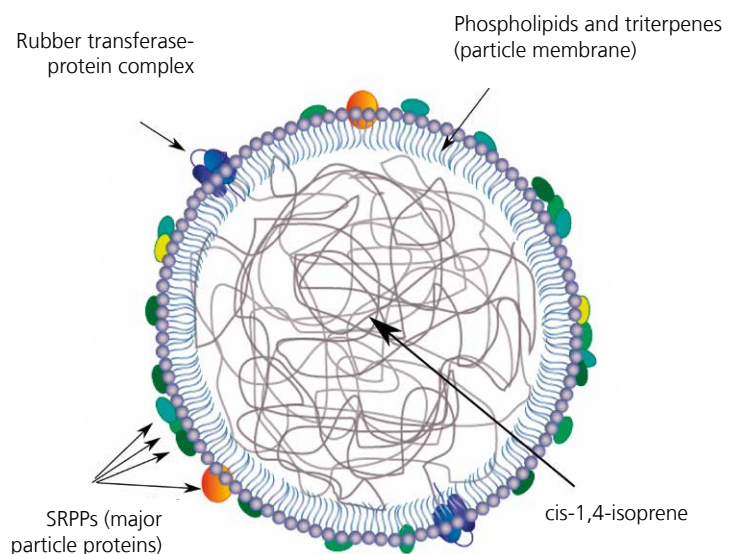
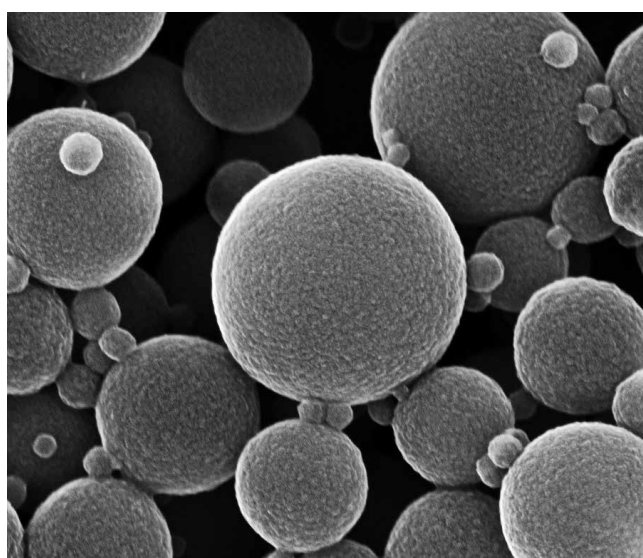


Figure 2 Scanning Electron Microscope (SEM) image of rubber particles under the electron microscope (left) and theoretical structure of a rubber particle with phospholipids and proteins (right).

negligible, suggesting the phospholipids and/or proteins were responsible for the observed effects.

Bioadditive isoprene rubber

Detailed characterization followed by the systematic addition of phospholipid mixtures to synthetic isoprene rubber showed clear effects on strain crystallization even when very small amounts (less than 1 percent of total rubber mass) of the defined mixtures were added.

A scalable manufacturing process was developed for these phospholipid fractions allowing larger quantities of the bioadditive isoprene rubber to be produced and used to prepare prototype truck tire treads at the Fraunhofer PAZ.

Once the protein extracts that had been separated from the natural dandelion rubber were characterized, a biotechnology-based concept was developed to produce the corresponding major proteins. This enabled the production of a sufficient quantity of proteins which could be incorporated into the

synthetic isoprene rubber. This also had a positive effect on strain crystallization.

Analysis: Biocomponents make natural rubber unique.

Bioadditive synthetic latex

Having demonstrated the positive effects of the phospholipid mixtures and proteins on the properties of synthetic isoprene rubber, the Fraunhofer IME also developed a laboratory method for the production of bioadditive isoprene latex. The addition of certain lipid mixtures was shown to have a considerable impact on the stability of the latex (Figure 4). Some additive effects were also observed when the proteins were present. An investigation of the strain crystallization of rubber samples derived from the latex again confirmed that the bioadditives were responsible for its enhanced properties. However, research

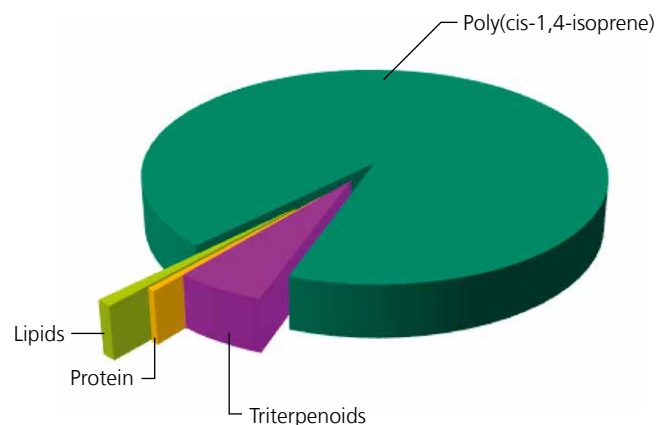


Figure 3 Phase separation of latex components (left) and their composition in dandelion rubber (right).



Expelling latex after wounding of a dandelion root.

focusing on bioadditive isoprene latex is still in its infancy and further more detailed investigation is required.

The cooperation between the Fraunhofer Institutes involved in the MAVO project has paved the way for the creation of a detailed application-relevant matrix that can be used with special lipids and proteins to optimize material properties such as strain crystallization in bioadditive isoprene rubber and latex. This means that different forms of rubber, containing different quantities of additives, can be optimized for different products.

Dandelion rubber 2.0

The high content of triterpenes in natural dandelion rubber means the process currently used to isolate natural rubber from *Hevea brasiliensis* is unsuitable for dandelions and must be modified. A strategy was developed to reduce the triterpene content of dandelion latex because these molecules do not play a significant role in strain crystallization and their removal improves the dynamic mechanical properties and processability of the natural rubber. The targeted disruption of triterpene

synthesis in the dandelion latex resulted in the production of dandelion rubber with much lower levels of triterpenes. A patent has been filed for the process and the resulting terpene-depleted natural rubber.

Biotechnological production of triterpenes/triterpenoids

From a pharmacological perspective, triterpenes/triterpenoids are diverse and interesting molecules that often show useful bioactivity. A patent has been filed for a biotechnological process developed at the Fraunhofer IME for the production of triterpenes/triterpenoids in baker's yeast (*Saccharomyces cerevisiae*) followed by purification. This results in high yields of very pure triterpenes in a short period of time, thereby enabling the production of samples for bioassays. |

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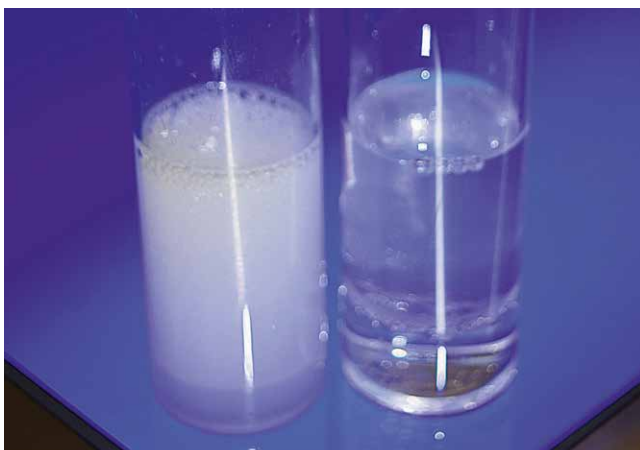


Figure 4 Comparison of protein-stabilized and instable latex (left) and pouring of a latex coating (right).

FROM NATURAL RUBBER TO BIOMIMETIC SYNTHETIC RUBBER

Synthesis of BISOYKA rubber on a pilot scale

Biomimetics involves research into and systematic transfer of natural phenomena to technological applications¹. The synthesis of BISOYKA, a biomimetic synthetic rubber, is therefore based on natural rubber. BISOYKA is mainly made up of polyisoprene (about 95 percent), which has a uniform microstructure and terminal groups. It is generally accepted that the biocomponents of natural rubber, such as proteins, terpenes and lipids, play a critical role in its good performance.

Optimizing the microstructure of synthetic polyisoprene: defect-free polymer segments that are 50 percent longer

A joint project has succeeded in producing polyisoprene with a high microstructure purity by means of coordinative polymerization. The project was conducted in the synthesis pilot plant at the Fraunhofer PAZ, which is run by the Fraunhofer IAP. The microstructure uniformity is linked to the high proportion of cis-1,4 double bonds which can be influenced by the

choice of catalyst. Parameters such as the choice of solvent, the reaction temperature and the ratio of co-catalyst to catalyst can also decisively influence the cis content². In addition to the proportion of cis-1,4 double bonds, controlling molar masses is also an important factor for processing. Adjustments can be made, for example, by regulating the polymerization temperature and the ratio of monomer to co-catalyst.

As shown in Figure 1, the choice of catalyst (commercially available, neodymium-based) influences the microstructure of polyisoprene. Nuclear magnetic resonance (NMR) spectroscopy was used to investigate the microstructure. The possible isomers of the isoprene (1,4-*cis*, 1,4-*trans*, 1,2 and 3,4) can be determined in the ¹³C-NMR spectrum. The proton NMR spectrum can be used to quantify the proportion of “defects” – here the percentage of 3,4-polyisoprene (1,2 does

COMPETENCIES

The Fraunhofer PAZ

At the Fraunhofer Pilot Plant Center for Polymer Synthesis and Processing PAZ, polymerization processes are transferred from the laboratory to pilot scale in the “Synthesis” department. This includes the analysis of polymerization processes (both from a chemical and process engineering perspective), upscaling, process design and engineering, implementation in the pilot plant as well as the safe and reliable multi-shift operation of the pilot plants. Spread over an area of 600 m², the synthesis plant has six pilot-scale polymerization lines (up to 880 L, operating conditions up to 100 bars/350 °C).

As a result of numerous successful projects with industrial partners and/or publicly funded projects, extensive know-how is on hand for converting batch polymerization processes into continuous polymerization processes as well as for designing and constructing experimental reactors up to semi-industrial scale.

Material development focuses on diene-based rubber and its various manufacturing technologies. The adjustment of the microstructure, the molar mass (distribution) and the introduction of functionalities into the macromolecule for optimum application performance are part of the development work, which also allows the production of samples ranging up to hundreds of kilograms.

The Fraunhofer PAZ is a joint initiative between the Fraunhofer IAP and the Fraunhofer IMWS.



Synthesis pilot plant of the Fraunhofer IAP at the Fraunhofer PAZ.

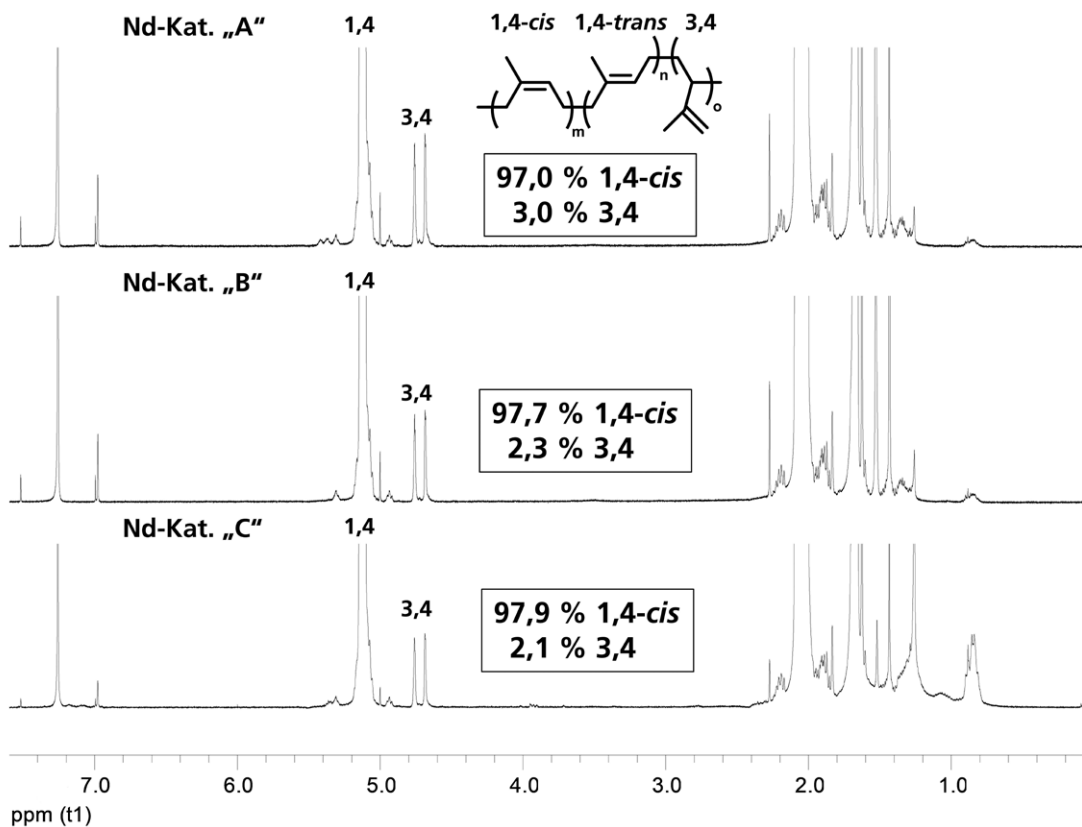


Figure 1 Superposition of $^1\text{H-NMR}$ spectra using an Nd catalyst system (A, B and C) and the resulting microstructure of the polyisoprene.

not occur) – and thus the proportion of 1,4-polyisoprene. Since no 1,4-*trans* polyisoprene formed according to $^{13}\text{C-NMR}$, the latter corresponds to the 1,4-*cis* content. While the fraction of 1,4-*cis* was only 97 percent when catalyst “A” was used, catalyst “C” resulted in a proportion of almost 98 percent. What appears at first glance to be a marginal increase is a milestone when it comes to strain-induced crystallization. Based on the statistical distribution of the defects, this improvement in the microstructure corresponds to 50 percent longer, defect free polymer segments!

The polymers were evaluated at the Fraunhofer IMWS with attention placed on strain-induced crystallization.

Here, investigations were conducted on the polymer films (crosslinked with peroxide) provided by the Fraunhofer IAP. This gave us direct feedback about the quality of the polymers with respect to strain-induced crystallization. We found that the use of the Nd catalyst system “C” generated improvements that came close to natural rubber, but still did not match it.

Introduction of functional end groups

Since natural polyisoprene has functional end groups in addition to a uniform microstructure, a further challenge was to introduce these into synthesized polyisoprene with a high microstructure purity. This matter was comparatively complex >

due to the catalyst structure and the postulated transfer mechanisms. High molecular weights also make it difficult to demonstrate the functionalization of the end groups, therefore a UV-active terminal group was chosen as the model system. Using gel permeation chromatography (GPC, otherwise known as size exclusion chromatography), unfunctionalized and end-functionalized polyisoprenes were measured with both an RI detector (concentration signal) and a UV detector. This method essentially separates the different polymer chains according to size. Thus, artifacts such as the physical mixing of the UV-active group with the polymer can be distinguished from the real binding of the UV-active group to the polymer chain. In the case of the non-functionalized polyisoprene (Figure 3a, "blank sample"), only signals from the RI detector are obtained, which means that, in these elution volumes, they are high-molecular compounds. The absence of the UV trace shows that the polymer chains do not have any UV-active groups. In contrast, signals are received by both detectors for the end group functionalized polyisoprene, which proves that these polymer chains carry UV-active groups.

BISYKA rubber contains the relevant biocomponents alongside functionalized polyisoprene that has a high microstructure purity.

Based on these findings, functionalization was then conducted with the actual end group, which is not UV-active, but whose chemical attachment to the still active polymer chains is chemically analogous. The group was selected on the basis of its natural counterpart in natural rubber, taking into account the postulated interactions with the bioadditives³. Thus, it was possible to obtain polyisoprene with a high microstructure purity and end group functionalization, whose strain-induced crystallization was improved, but was still below that of natural rubber. In a further phase of the project, bioadditives provided by the Fraunhofer IME were

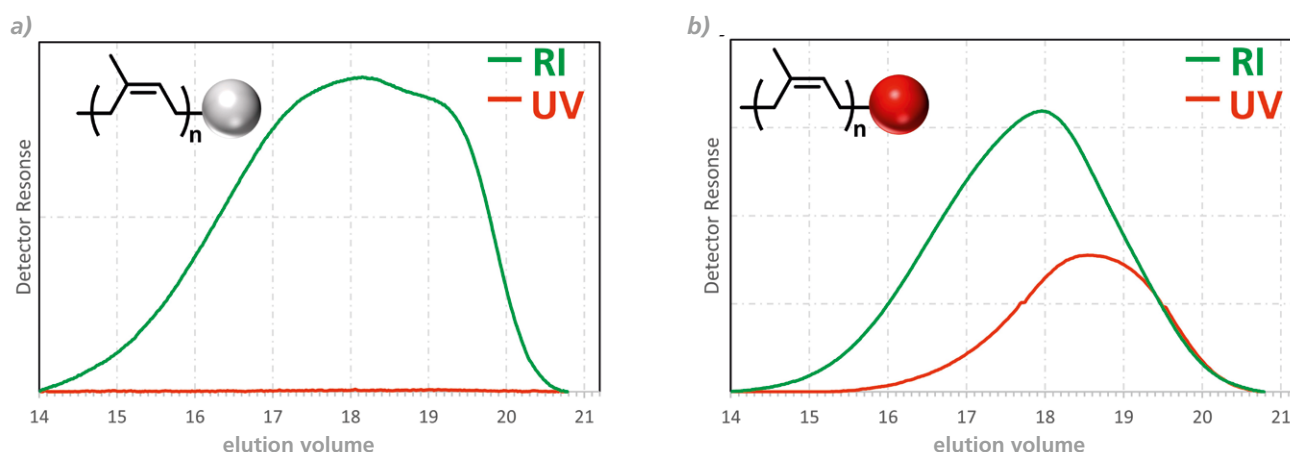


Figure 3 GPC curve (elution volume) of a) non-functionalized polyisoprene ("blank sample") and b) polyisoprene functionalized with a UV-active heteroaromatic compound.

*Material development
in a lab reactor.*



mixed into the polyisoprene synthesized at the Fraunhofer PAZ in a screening series.

The polymer films crosslinked with peroxide were investigated at the Fraunhofer IMWS. Additivation of one particular group of bioadditives showed significant positive effects with respect to strain-induced crystallization and a bioadditive component could be selected from this group in a further screening series.

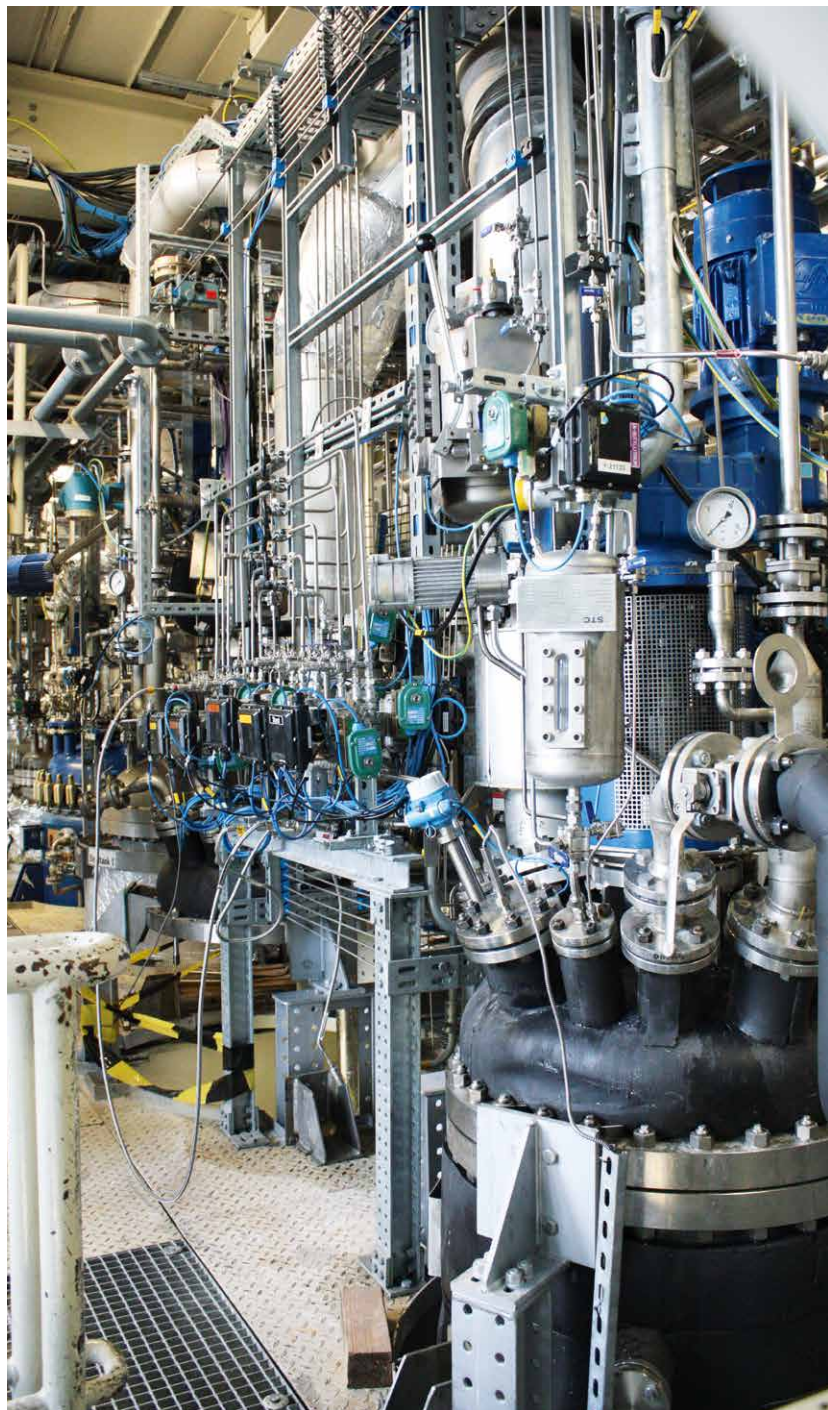
Transfer to a semi-industrial scale

After considering all the parameters, the synthesis of the highly microstructure-pure polyisoprene, which was optimized in line with the project objectives, was upscaled from the laboratory to the pilot plant and thus to a double-digit kilogram scale. Polymerization and end group functionalization was carried out with the process parameters generated in the laboratory in the 600 L stainless steel pressure reactor C2110. The biocomponents were mixed in at a later stage of the process, which was decisive for property generation. Then a process patented by the Fraunhofer IAP/PAZ was used to separate the product from the solvent using medium-pressure steam. In a final step, the product underwent convective drying.

As a result, the biomimetic synthetic rubber BISOYKA, for which a patent has been filed, can be produced on a scale required by tire tread compounds. The performance of the BISOYKA tire was compared to that of a natural rubber tire in a practical test. |

Authors:

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Rubber synthesis on a pilot scale (600 L reactor).

NOVEL SILICA FILLERS FOR THE RUBBER AND TIRE INDUSTRY

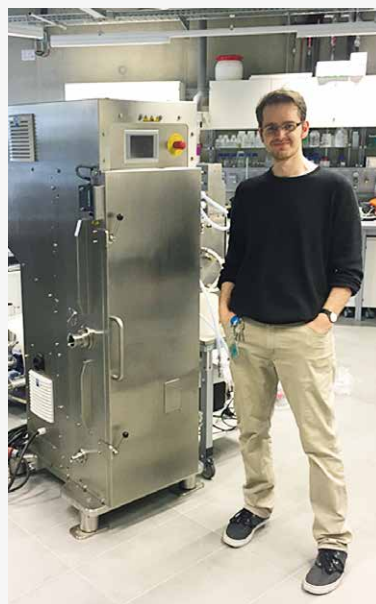
Interaction between fillers and matrix

COMPETENCIES

The Fraunhofer ISC

The Fraunhofer Institute for Silicate Research ISC is specialist in the development and manufacture of innovative micro- and nanoscale particles and functional fillers in the fields of energy, the environment, mobility, safety and health. In general, these particles made by wet-chemical processes have a complex architecture and combine several functional units. Traditionally, the Fraunhofer ISC research and development has focused on silica and its application as functional filler and coating additive, while magnetic particles for water purification, perovskites for solar and photocatalysis, and 2D particles for flame retardancy are also gaining increasing importance.

The Fraunhofer ISC regards itself as an intermediary for the nano world. Therefore, the scale up of the synthesis processes is crucially important. Finding ways to increase batch sizes and transitioning to semi-continuous and continuous processes are both part of its day-to-day business.



Scale-up equipment with 100 L batch reactor (left), semi-continuous centrifuge (center) and a pilot-scale spray dryer (right).

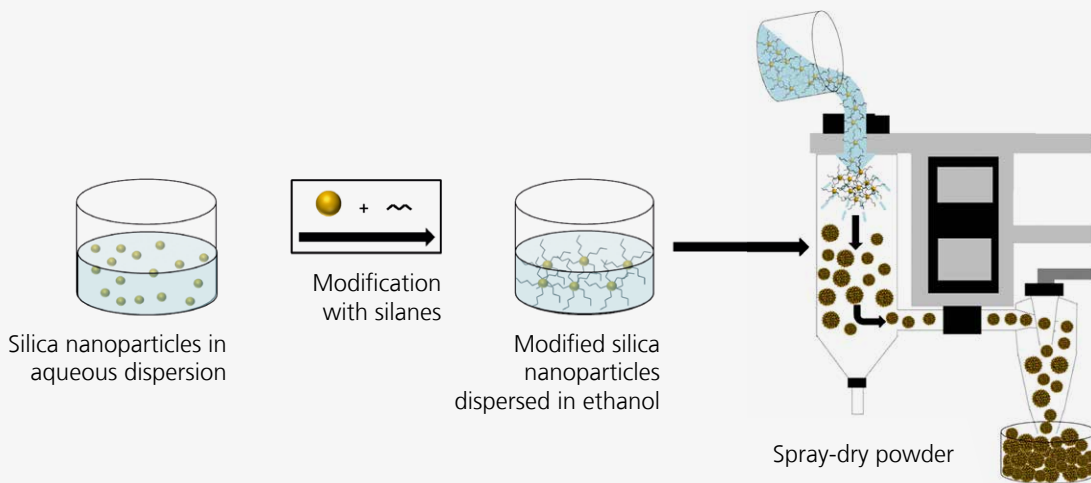


Figure 1 Modification of colloidal silica nanoparticles with silanes and subsequent spray-drying to produce microscale powders².

Silica fillers for the tire industry

Silica (silicon dioxide) has become an important raw material for the rubber and tire industry and an indispensable component of modern high-performance formulas. Silica fillers have revolutionized tire development over the past twenty years by breaking or expanding the “magic triangle” of the long-established and seemingly insurmountable mutual limitation of properties with carbon black as the sole reinforcing filler. This has made it possible to reduce the rolling resistance of the tires compared to those made with carbon black. At the same time, abrasion resistance has been maintained and wet grip has improved¹.

Silica fillers in natural rubber

The use of highly dispersive silica nanofillers in combination with silanes such as Si69® for solvent-polymerized synthetic elastomers S-SBR (solution styrene-butadiene rubber) and BR (butadiene rubber) is an established standard practice. However, silica fillers still play a minor role in natural rubber (NR). This is because the interaction between rubber, bonding agent and fillers does not function properly and/or is still ineffective. This deficit of natural rubber is attributed to the presence of considerable amounts of non-rubber components, such as proteins, carbohydrates and lipids, which massively influence and disrupt the dispersion and bonding of silica fillers in rubber.

The use of silica fillers in natural rubber therefore remains the subject of ongoing research. Focus is on the controlled dispersion of nanoscale or nanostructured particles in the rubber matrix, which is regarded as essential for the quality and functional behavior of the tires made from it. Efforts are going so far as to investigate the *in-situ* production in the rubber matrix of silica particles from liquid precursors in a sol-gel process.

Approach of the Fraunhofer ISC: fillers with controlled dispersion behavior

Within the framework of MAVO BISYKA, the Fraunhofer ISC has developed an alternative approach that uses colloidal silica nanoparticle dispersions to produce nanostructured microparticle powders with – adjustable dispersion behavior. These particles have the potential to be arranged in the rubber either in mechanically stable aggregates or loose agglomerates or to be separated into their initial/primary particle size. In contrast to the long-established rubber processing technique in which the silanization reagent is immediately added together with the filler and reacted *in-situ*, the Fraunhofer ISC process adjusts the behavior in advance under controlled conditions. This produces previously unattainable precision when adjusting the agglome-

Colloidal silica nanoparticles enable previously unattainable precision in adjusting agglomeration and aggregation behavior.

ration and aggregation behavior and, hence, the reinforcing effect of the fillers. It is also easier to control the proteins and lipids competing for the surface positions on the fillers when they are incorporated into the natural rubber.

At the center of the new approach is an optimized silanization protocol for which a patent has already been submitted. This can be used to directly and very efficiently silanize commercial, alkaline stabilized, aqueous, nanoparticulate silica dispersions (colloidal silica, e.g. Köstrosol 2040, Chemiewerke Bad Köstritz) without prior solvent replacement. Decisive is >

Figure 2 Scanning electron microscope images of spray-dried granules with various degrees of modification starting from 0 for non-modified to 1 for completely silane-modified (scale bar: upper row: 2 μm ; lower row: 100 nm)³.

that the particles still exist as primary particles after modification with silane. This synthesis procedure works for non-reactive silanes whose effectiveness is based primarily on hydrophobizing the particle surface (e.g. octyltriethoxysilane, OCTEO) as well as for reactive silanes that bring about covalent coupling of the fillers to the rubber matrix (e.g. Si69[®], Evonik AG).

The particles are dried in two stages, by spray-drying with subsequent post-drying in an oven. Spray-drying not only serves to remove the dispersion medium (mainly water and ethanol), but also functions as a shaping process, giving the fillers their shape and combining them to form microscale granules that are preferably spherical and typically 2 to 20 micrometers in diameter. Depending on the type and quantity of the particles and silanes used, micro-scale powders with nanoscale substructures are obtained which act as predetermined breaking points. They determine the dispersion behavior of the fillers both in

liquids and in the rubber matrices (Figure 2). The powders can be conveniently stored and used as bulk materials as required.

A quick orientation of the particles' surface properties is obtained through dispersibility investigations in which the particles are incorporated into liquids of different polarities (Figure 3). Complete wettability and low turbidity are indicators of a good modification and boundary layer compatibility. This enables rough general statements to be made, such as whether they are hydrophilic or hydrophobic, and intermediate stages can be determined as well. The method also gives an indication of how accurately and reproducibly the silanization works⁴.

Potential applications for the new silica fillers with adjustable dispersibility

Improved control over dispersibility makes it possible to simulate, analyze and optimize the various ways the filler-

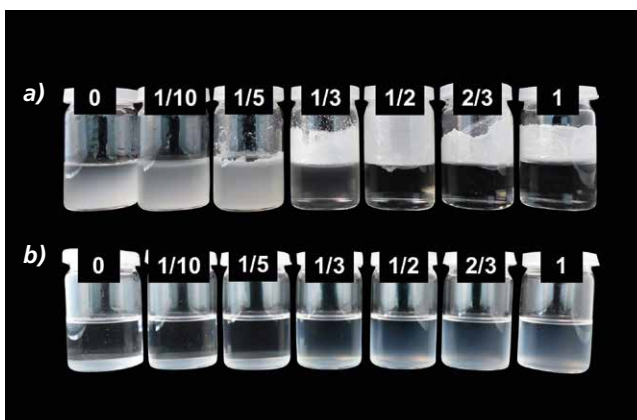


Figure 3 Dispersibility of particles with different degrees of modification (0 for non-modified to 1 for fully modified) in liquids of different polarity (a) water and (b) toluene^{3,4}.

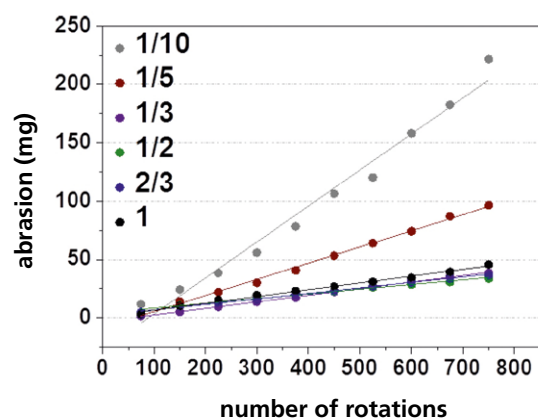
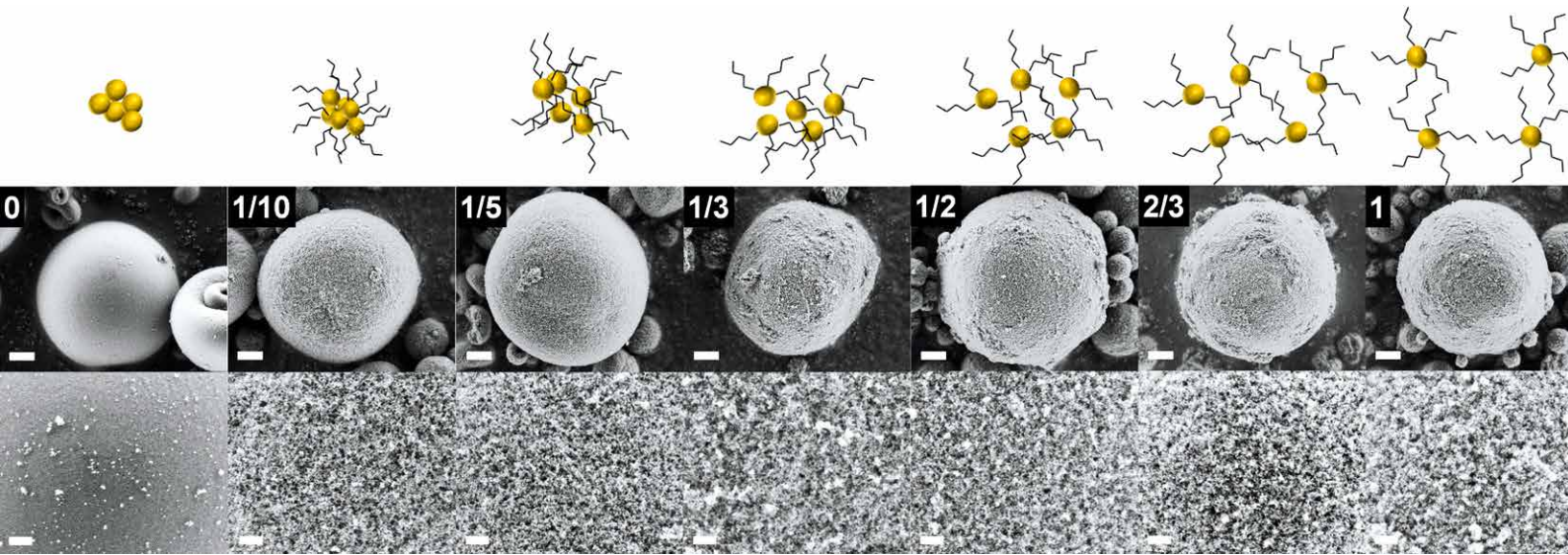


Figure 5 Cumulative abrasion of a rubber composite as a function of the length of abrasion (number of revolutions). As OCTEO coverage of the filler increases, overall abrasion goes down. Measurements performed by the Fraunhofer IWM³.



related reinforcing effects contribute to the rubber composites. For example, by simply adjusting the type and quantity of silane used and thus the degree of dispersion and bonding of the fillers, it is possible to adjust the properties of a rubber composite (storage modulus, tensile strength, abrasion) even when the filler proportions remain unchanged. Figure 4 shows an example of how the amount of silane (OCTEO) influences the storage modulus of rubber composites. It shows that the system reacts very sensitively to the silane coverage. Interestingly, when a hydrophobizing silane is used, the storage modulus and the influence of the filler network continuously decrease as coverage increases.

Conversely, as OCTEO coverage increases, there is a steady increase in abrasion resistance and/or reduction in cumulative abrasion until there is no further change after a modification degree of 1/3 (Figure 5).

The new particles are not regarded as substitutes for the existing silica fillers. Instead they are seen as additives and dispersing aids that achieve a better control over the proteins and lipids competing for the surface areas when they are incorporated into natural rubber. |

Authors:
Dr. Claudia Stauch, Thomas Ballweg

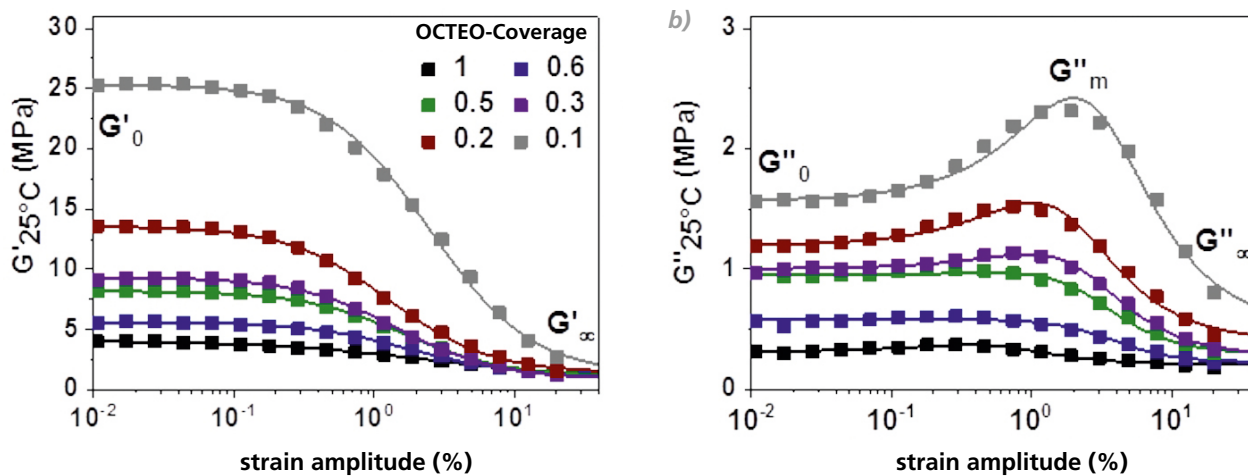


Figure 4 Storage modulus G' (left) and loss modulus G'' (right) as a function of the strain amplitude for IR-silica composites consisting of 90 phr spray-dried silica-NP at different degrees of modification. Measurements performed by the Fraunhofer IMWS³.

ELASTOMER CHARACTERIZATION

New methods for analyzing abrasion resistance

The service life of elastomer components is often determined by their abrasion resistance: tires have to be changed when the tread is worn out and conveyor belts are subject to wear and tear when they come into contact with guides and scrapers. Complex practical tests are often the only way to assess the abrasion resistance of a component, for example by testing newly developed tires on the road. During material development, however, it is preferable to obtain initial information on abrasion behavior using small samples and accelerated measuring procedures.

Wear of elastomers through fatigue crack growth

Various mechanisms are under discussion as causing elastomer wear. For example, a high local mechanical load can cause wear when a fragment is torn off the tire of an off-road vehicle after it comes into contact with a sharp edge. In contrast, the tread of a rolling tire is subject to moderate

fatigue stress due to slip, which causes fatigue cracks. This, in turn, leads to particle detachment and wear. In addition to mechanical loads, (tribo)chemical effects – such as the degradation of the elastomer through ozone – can also lead to wear.

In order to simulate these wear mechanisms in lab experiments, various test configurations were developed, for example the “cut-chip-chunk” configuration that simulates harsh loads experienced by off-road tires, or the LAT100, which is able to determine abrasion as well as other application properties of tires under various loading regimes.

Since the wear of a rolling tire is primarily determined by fatigue wear, we developed a modification of the blade abrasion test, a method used to investigate abrasion caused by fatigue¹. In this test, a sharp blade sweeps the elastomer

COMPETENCIES

The Fraunhofer IWM

The Fraunhofer Institute for Mechanics of Materials IWM is a research and development partner for industry and public contracting bodies concerning the topics of component and systems reliability, safety, durability and functionality. The Fraunhofer IWM’s “mechanics of materials” approach is used to identify weaknesses and defects in materials and components, determine their causes and develop solutions that lead to the safer use of components as well as the development of functional materials and resource efficient manufacturing processes. The MicroTribology Centrum μ TC conducts research into friction and wear. Employees at the μ TC optimize tribological systems and develop solutions to reduce friction and protect from wear and tear using technical ceramics, innovative lubricants, tribological coating systems and tribological materials that are adapted for manufacturing. Experimental investigations, multi-scale modeling, numerical simulations and microstructure analyses examine friction, abrasion, run-in and wear mechanisms.



Friction partner with three steel balls.

surface. This creates grooves on the surface that are perpendicular to the direction in which the blade slides. The repeated scoring of these structures causes a fatigue load on the grooved structure which leads to the formation of fatigue cracks and the detachment of particles, i. e. wear and tear of the surface. We replaced the blade with three rigidly mounted steel spheres² which slide in a circular motion over the elastomer surface (see Figure 3). This loading regime also creates a ridge structure and material abrasion due to fatigue cracks. However, unlike when there is contact with a blade, the stress caused by the spheres on the elastomer sample can be more precisely adjusted and better analyzed through finite element simulations.

A tribometer for measuring abrasion is shown in Figure 2. Flat elastomer panels measuring $40 \times 40 \times 2 \text{ mm}^3$ are used as samples. Dead weights apply pressure between the spheres

and sample surface pressing the friction partner against the rotating sample from above. After a defined number of rotations, the sample is weighed to determine abrasion. During the measurements, a torque sensor is used to measure the friction torque and a probe assesses the vertical position of the friction partner.

Measurements on tire compounds

Figure 3 shows the increase in cumulative abrasion as a function of the number of revolutions for different elastomer compounds. In general, there is a linear increase in cumulative abrasion as the number of revolutions increases (i. e. as the friction path and/or the number of alternating loads increases). The wear resistance of the elastomer can be determined based on the cumulative wear after a defined number of revolutions or by means of the slope of the line of best fit (see Figure 4). The slope of the line of best fit corresponds to the wear rate >

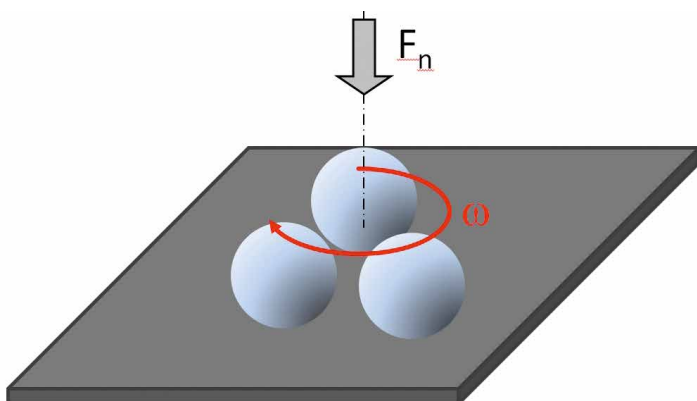


Figure 1 Illustration of the loading arrangement.

BISYKA rubber reaches
the abrasion
resistance of natural rubber.

in the “run-in” state because it does not take into account run-in phenomena – an initially higher or lower loss of mass described by the y-axis intercept of the regression line.

In the abrasion tests, the differences between the optimized tire compounds (“NR tread” and “BISYKA tread”) and the non-optimized laboratory samples (“SVR-10”, “PIP-90”, “Ski-3” and “NATSYN”) become clearly visible. The non-optimized laboratory samples are expected to have a higher abrasion than the optimized tire compounds. In order to evaluate the results of the abrasion tests, a tire’s real tribological load should be compared with the tribological load of the samples in the experiment².

In the tests, the balls were loaded with a normal force of $F_n = 60$ N. This amounted to about twice the pressure exerted on a typical truck tire. At 60 revolutions/minute,

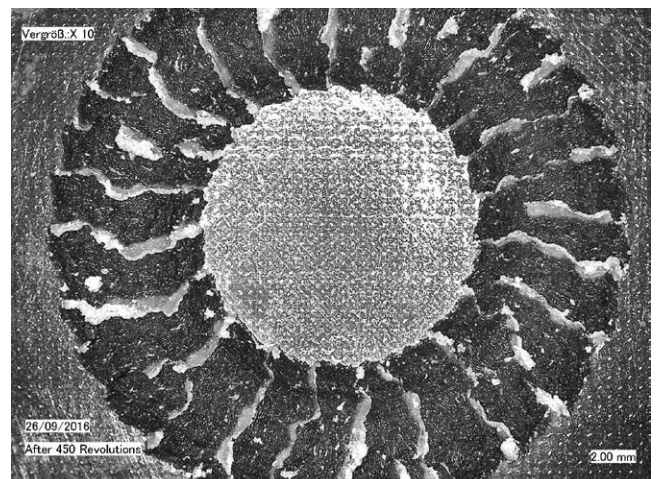


Figure 2 Tribometer for determining elastomer wear (above), ridge structure in the wear scar of an unreinforced elastomer (center), profile of a wear scar of a tire compound (below).

the slip velocity in the abrasion tester corresponded to the approximate slip velocity of a tire rolling straight ahead at a speed of 90 km/h. The longitudinal slip after 15,000 revolutions of the abrasion tester corresponded to the longitudinal slip of a rolling tire after a distance of 50,000 km. Measurements of an elastomer compound used for truck tire treads revealed that the abrasion in the tribometer is approximately 10 times less than the abrasion one would expect during normal operation. This is plausible if one takes into account that the increased abrasion caused by acceleration, braking or cornering and by abrasive loads caused, for example, by rough road surfaces, are not simulated in this experimental configuration.

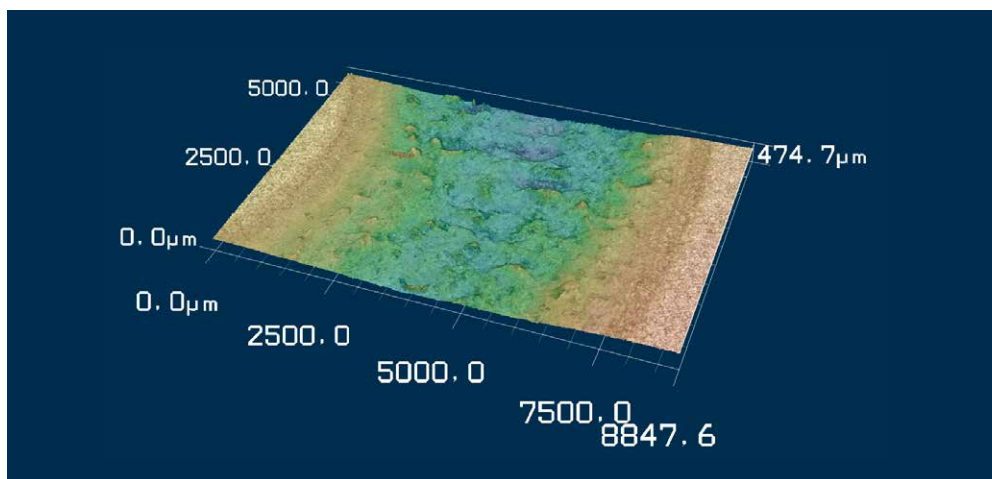
Summary and outlook

The measurement methodology developed at the Fraunhofer IWM to investigate fatigue wear allows elastomer

samples to be examined under tribological conditions that correspond well to the typical fatigue load that tires experience "on the road". Initial investigations on different tire compounds showed that the methodology is able to differentiate well between different elastomer compounds.

Only a small amount of material is required for a measurement due to the small sample size, so the methodology is ideally suited, for example, for testing an elastomer compound during its developmental phase. A comparison of the measurement results with other measurement methods established in the industry (e.g. abrasion measurements according to DIN 4649 or measurements using LAT 100 according to Grosch) is the subject of current research.

A further development of the abrasion tester will enable wear to be measured continuously. A probe is used to determine >



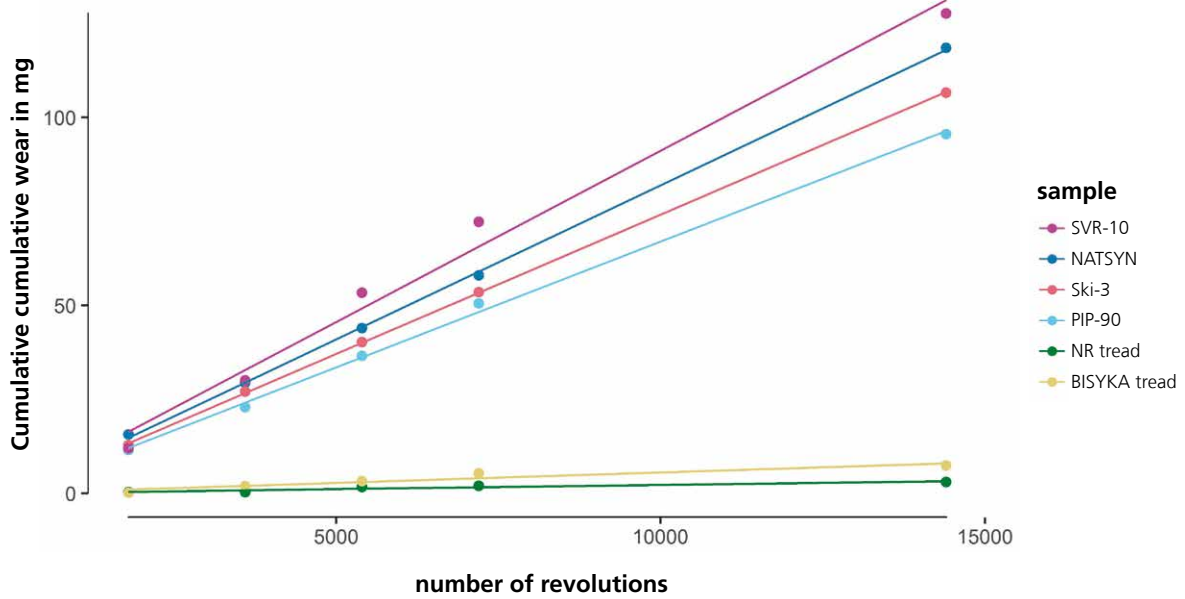


Figure 3 Cumulative wear of various tire compounds. To facilitate the comparison of the different specimens, the y-axis intercept (which describes the run-in behavior behavior) was subtracted from the data.

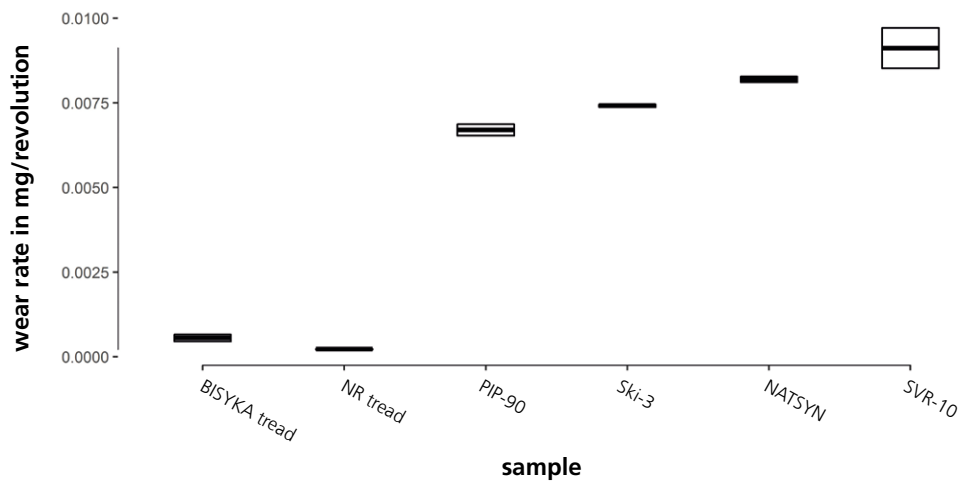


Figure 4 Abrasion rate in broken-in state for various tire compounds.

the vertical position of the friction partner from which, ideally, the depth of the wear scar can be measured over time on a continuous basis.

However, the vertical position of the friction partner does not only depend on the depth of the groove. The thermal expansion of the sample and the apparatus generated by the frictional heat as well as vertical deformations of the elastomer sample caused by its stress state (e.g. by the frictional torque) influence the z signal. If, however, the system reaches a stationary thermal and mechanical state, the input of thermal expansion and mechanical strokes remains constant allowing wear to be continuously measured by evaluating the z signal. In the measurement shown in Figure 5, this stationary state is reached after 10,000 to 15,000 revolutions; the change in the z signal then describes

the formation of the wear scar. Measurements of different elastomer samples showed a good correlation between the change in z-signal and the wear rate, which results from the gravimetric analysis of the abrasion. It is particularly advantageous to use the vertical position of the friction partner to continuously measure abrasion if repeated removal and cleaning of the sample for weighing is not desirable or possible. This occurs, for example, when measurements have to be taken in a specific atmosphere, for example in an inert or oxidative atmosphere, in order to investigate the influence of chemical degradation of the elastomer on abrasion, or if abrasion is to be investigated under the influence of various substances (e.g. water, lubricants). |

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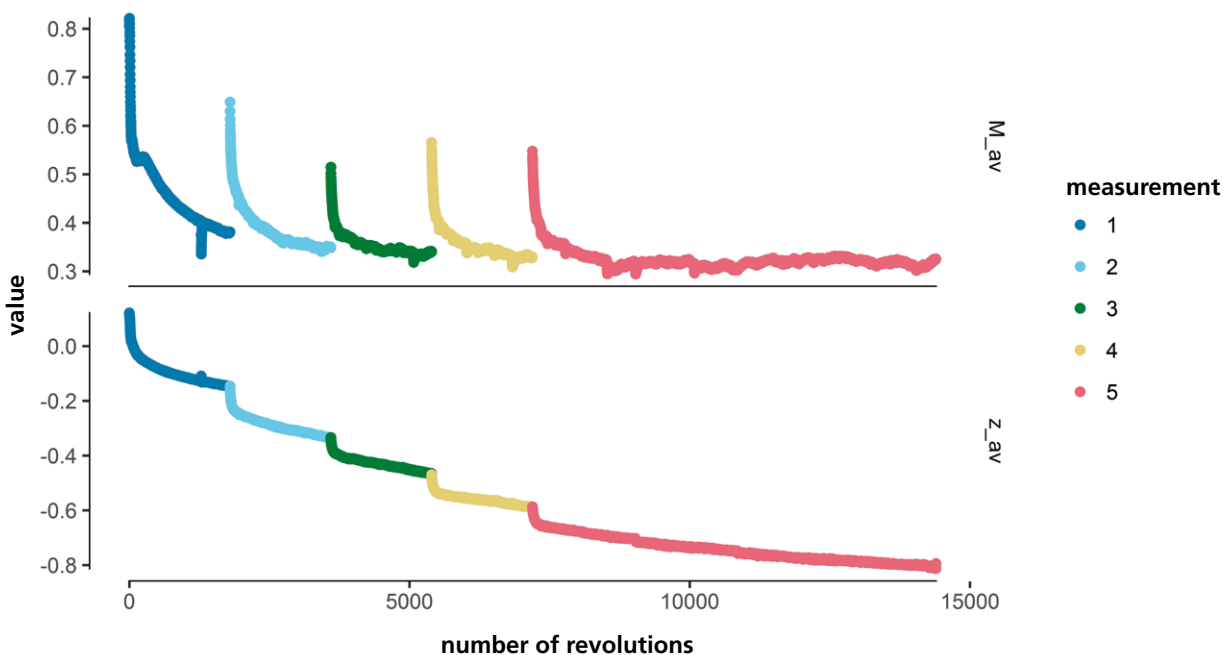


Figure 5 Mean friction torque M_{av} in Nm (above) and mean vertical position z_{av} in mm (below) for a measurement of the material PIP-90.

STRAIN-INDUCED CRYSTALLIZATION AS A CRITERIA OF MATERIAL OPTIMIZATION

An indicator for evaluating abrasion resistance

One of the outstanding properties of natural rubber is its capacity to undergo strain-induced crystallization. If a cross-linked natural rubber sample is uniaxially stretched, the first signs of crystalline rubber components can be found at about 200 percent elongation. Above this critical strain, at which strain-induced crystallization begins, the crystalline component in natural rubber usually increases almost linearly with elongation. At an elongation of 500 percent, a degree of crystallization D_c of roughly 10 percent is typically achieved. The value depends on additional parameters such as the cross-linking density. Interestingly, strain-induced crystallization is reversible, i. e. the degree of crystallization decreases again when the strain is subsequently reduced. In natural rubber composites containing fillers, the strain-induced crystallization of the natural rubber matrix starts earlier and achieves relatively higher degree of crystallization. This can be explained by a

localization of the strain through the filler particles, i. e. the local strain clearly exceeds the macroscopically measured strain of a test specimen. An application-relevant consequence of strain-induced crystallization is that crack propagation is hindered because crystallization occurs at the crack tip due to high local strains, which leads to a kind of self-reinforcement of the natural rubber matrix in this critical region.

Despite decades of extensive research on the subject, the molecular causes of strain-induced crystallization of natural rubber are still not fully understood. It is clear that an extremely high stereoregularity of polyisoprene chains in natural rubber (cis-1,4 content $\gg 99\%$) is an important requirement for strain-induced crystallization. Synthetic polyisoprene samples with significantly lower cis-1,4

COMPETENCIES

The Fraunhofer IMWS

The Fraunhofer Institute for Microstructure of Materials and Systems IMWS is dedicated to activities in the area of materials research for various material classes and markets. Polymer research activities in the business unit Polymer Applications focus in particular on thermoplastic systems for lightweight construction and elastomers. In the field of elastomers, its Halle site offers various methods to characterize the properties of rubber composites using mechanical testing methods – from traditional tensile tests to highly specialized dynamic measurement methods, imaging methods for various length scales and calorimetric and (di)electrical testing methods. The activities focus on the elucidation of process-structure-property relations and on a better understanding of the molecular origin of reinforcement and dissipation. This understanding of materials is utilized in cooperation with material manufacturers, tire manufacturers and tire retreaders to efficiently optimize rubber compounds for tire treads. In addition to tires, other important fields of activity are thermoplastic elastomers and rubber recycling. By 2020, the Fraunhofer IMWS will have significantly expanded its capabilities in the field of elastomer processing at its Schkopau site and will have a mixing hall with pilot-scale tandem mixer for processing rubber compounds.

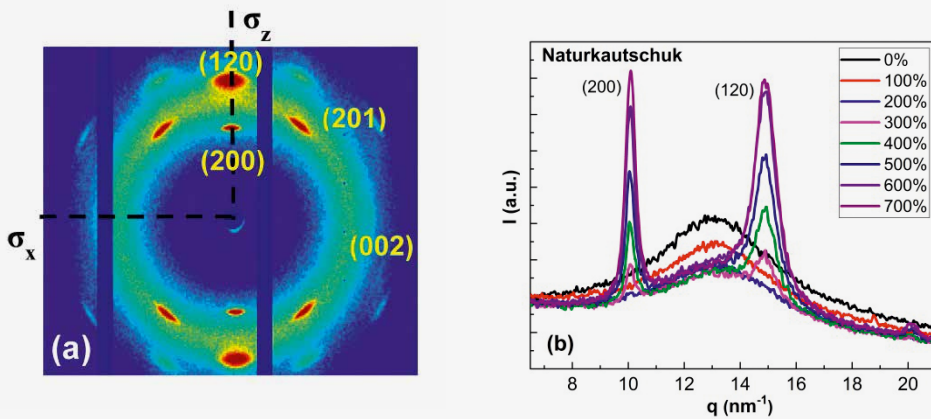


Figure 1 2D diffractogram at 300 percent horizontal elongation (a) and a 1D diffractogram at different elongations for partially crystalline natural rubber (b).

proportions (< 95 %) do not crystallize under strain or only to a very small extent. Synthetic polyisoprenes with higher cis-1,4 proportions (95 – 98 %) often exhibit strain-induced crystallization but fall far short of the degree of crystallization identified in natural rubber. In addition, the critical strain which triggers the onset of crystallization is always significantly higher than for natural rubber. The extent to which this involves the microstructure of the polyisoprene chains in natural rubber or the biological additives in natural rubber remains the subject of current scientific discussion. The nucleating role of bioadditives in natural rubber is one obvious assumption. One key research topic of the BISKYA research project was to better understand which of the other biological components in natural rubber are crucial for strain-induced crystallization.

Methods for determining strain-induced crystallization

In order to evaluate the strain-induced crystallization of novel rubbers based on synthetic polyisoprene, a special measuring set-up was developed in the laboratory that allows relative degree of crystallization to be determined as a function of static strain. When determining the relative degree of crystallinity, a fairly simple and robust method was used which is based on the characteristic peaks in the X-ray diffractogram. A two-dimensional diffractogram of natural rubber in the semi-crystalline state at 300 percent static strain (Figure 1a) shows peaks occurring in different directions relative to the uniaxial direction of strain. The method used for material screening in the BISKYA project focuses on the peaks observed in the detector plane that are orthogonal to the strain direction. These are the reflexes indicated at (200) and (120). This simplification allows the relative degree of crystallization under static strain to be determined by means of a standard BRUKER D8 ADVANCE diffractometer. The only other requirement was the construction of a special automated strain measuring cell which allows the rubber samples under investigation to be stretched horizontally to up to 750 percent. The measuring setup is shown in Figure 2. One-dimensional diffractograms containing the scattering intensity

orthogonal to the strain direction are detected (Figure 1b). The intensity of the amorphous halo and crystal reflexes is then determined through integration to determine relative degrees of crystallization. The relative share of the intensity of the crystalline reflexes is used as the relative degree of crystallinity $D_{c,rel}$ in order to evaluate the strain-induced crystallization of various polyisoprene-based materials.

One of the outstanding properties of natural rubber is its capacity to undergo strain-induced crystallization.

Although $D_{c,rel}$ is not an absolute degree of crystallization, this value was successfully used to determine and optimize strain-induced crystallization in polyisoprene-based rubbers and compounds. Obviously, the assumed proportionality of $D_{c,rel}$ to the absolute degree of crystallization is a good approximation since the anisotropy is largely unrelated to the sample. This assumption significantly lowers the experimental effort required to evaluate the crystallization capacity of novel rubbers and compounds under static strain.

Optimizing the strain-induced crystallization of polyisoprene-based rubbers

The central goal of the BISKYA project was to maximize the strain-induced crystallization of polyisoprene-based rubber systems. As already mentioned in the corresponding chapters, the Fraunhofer IAP produced polyisoprenes with a high cis-1,4 content and special end group functionalization. The Fraunhofer IME investigated and prepared special bioadditives in order to evaluate the significance of various influencing factors on strain-induced crystallization. Since the substances being screened were often only available in relatively small quantities, they were first mixed with a solution and then



“Its excellent properties in terms of strain-induced crystallization are accompanied by the excellent abrasion resistance of the BISIYKA compound. This was demonstrated by the abrasion test in the laboratory and in the final tire test.”

Prof. Dr. Mario Beiner, Fraunhofer IMWS

with a peroxide crosslinking system. Subsequently, solution cast films were produced from these on a gram scale which were cross-linked under standard conditions after careful drying. This made it possible to systematically evaluate a large number of rubber systems with a wide variety of polyisoprene and bioadditive components and to compare them using the method described above for monitoring strain-induced crystallization. Figure 3a shows some examples of the dependence of the degree of crystallization on static strain. It can be seen that end group functionalization and bio-additivation significantly impacts strain-induced crystallization. By systematically varying the components and the composition, the strain-induced crystallization could gradually be optimized in rubber systems that are based on synthetic polyisoprene. Components that appeared suitable were upscaled to produce larger quantities of biomimetic synthetic rubber. The crystallization properties of this BISIYKA rubber are compared with those of traditional natural rubber in Figure 3b. It is apparent that the onset of strain-induced crystallization in BISIYKA rubber occurs at higher strain values, but at high strains

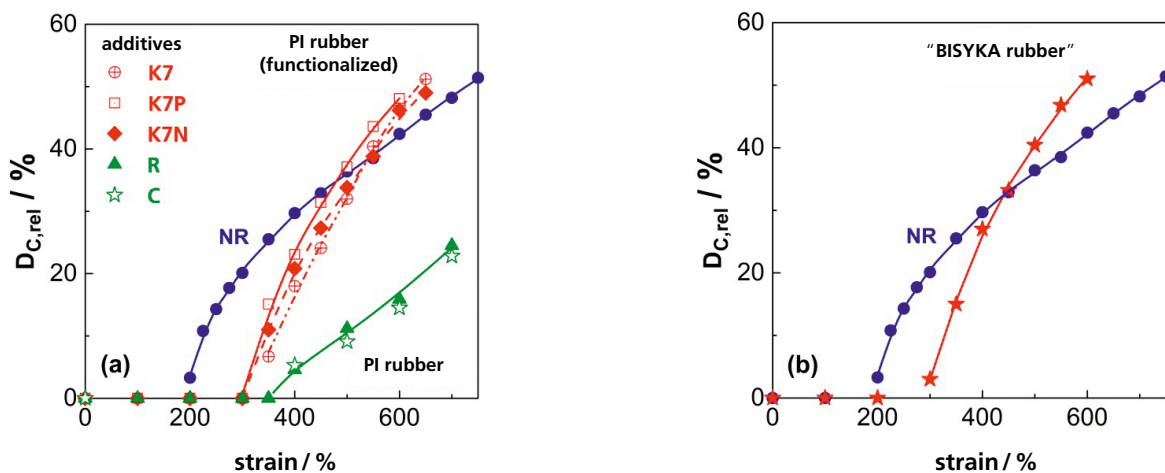


Figure 3 Relative degree of crystallization $D_{c,rel}$ for (left) various peroxide-cured rubber systems based on bioadditive and partially end-functionalized polyisoprenes and (right) the sulfur-cured BISIYKA rubber used in the production of tire compounds.

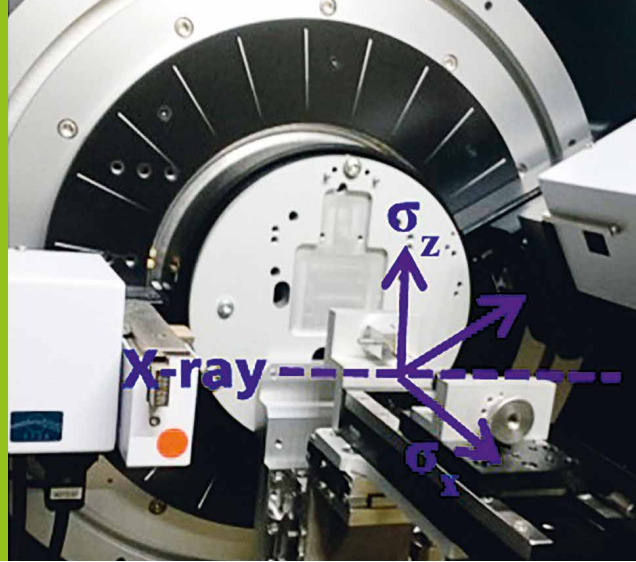


Figure 2 The measuring set-up developed by the Fraunhofer IMWS.

achieves higher relative degrees of crystallization than for the identically crosslinked natural rubber analyzed as the reference system. In the final step, the strain-induced crystallization of the sulfur-crosslinked compounds used in the tire test was characterized. These compounds had a carbon black content of 50 phr. In addition to 70 phr of natural or BISIYKA rubber, they also contained 30 phr butadiene rubber. The corresponding diffractograms are shown in Figure 4. The BISIYKA compound also exhibits comparable degrees of crystallization and does not lag far behind that of the natural rubber-based reference compound. Abrasion tests in the laboratory and final tire tests demonstrate the outstanding properties of strain-induced crystallization in conjunction with the excellent abrasion resistance of the BISIYKA compound, which is presented in the concluding chapter. |

Authors:

Dr. Gaurav Gupta, Prof. Dr. Mario Beiner

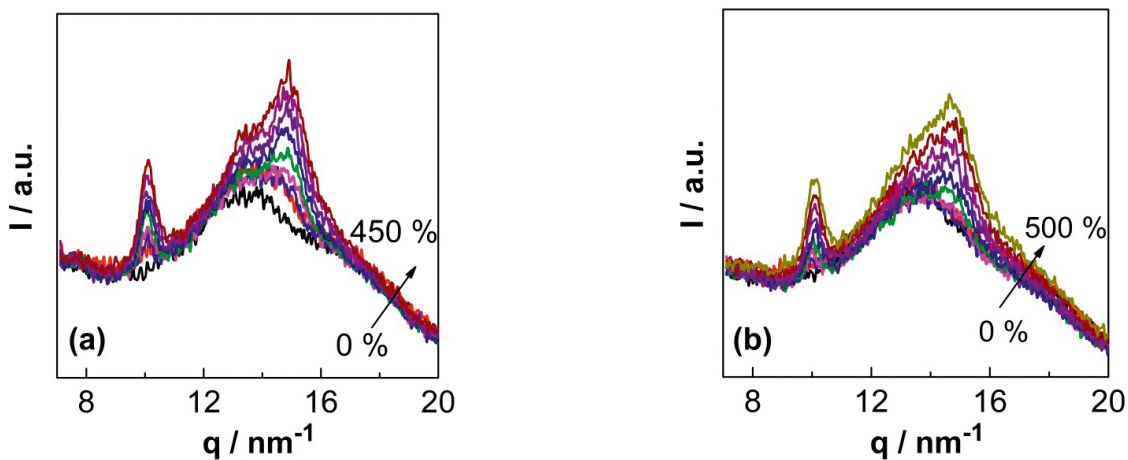


Figure 4 Diffractograms for sulfur-cured rubber components with a carbon black content of 50 phr, which, in addition to the 70 phr (left) natural rubber and/or the BISIYKA rubber (right), also contain 30 phr butadiene rubber. The relative degrees of crystallization $D_{c,rel}$ at 450 percent elongation are 33.6 percent for the natural rubber-based reference compound and 30.6 percent for the compound based on BISIYKA rubber.

BISYKA TIRE COMPOUND IN A PRACTICAL TEST

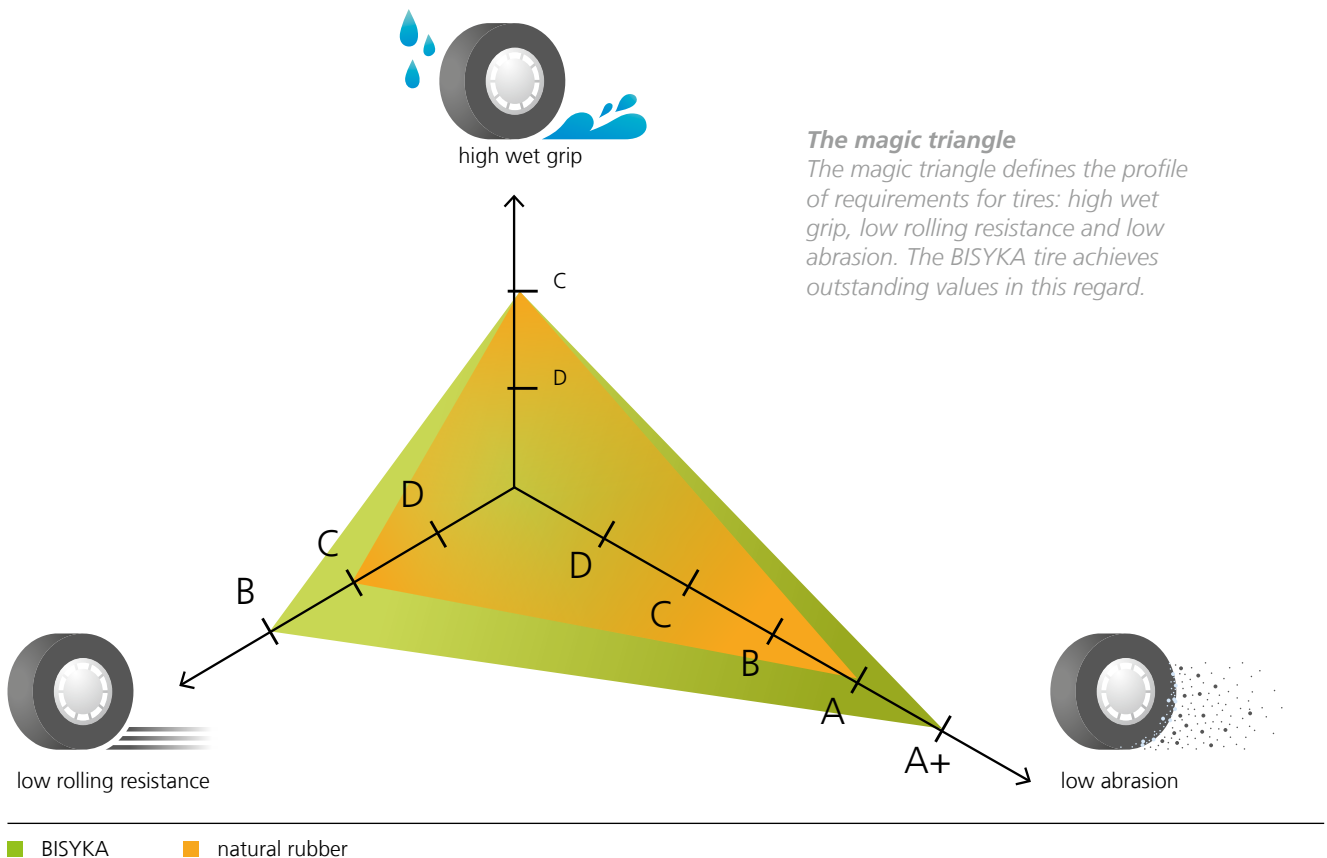
Assessment by independent partner

Four tire demonstrators (for passenger cars) based on the synthesized BISYKA rubber were produced with a truck tread compound. Testing truck tires is much more complex than testing its passenger car equivalents. Despite the geometric differences, tests on car tires provide results that enable a good assessment of the properties of the tire materials. This allowed us to carry out initial realistic application tests on BISYKA rubber.

Selection and production of tire tread compounds

MARANGONI Retreading Systems Deutschland GmbH – a Fraunhofer partner from a successful joint project – was

recruited to select and produce suitable tread compounds for comparative tire tests. Involving MARANGONI meant that the selection of compounds for the tire tests was backed by many years of know-how in the field of truck tire compounds. This also meant we had access to the mixer sizes and configurations required for processing the rubber compounds for the demonstrator tires. Thus, processing problems could be ruled out from the start. Two carbon black-filled compounds were produced according to a recipe tested for truck treads. The basic formula, containing 70 phr of natural rubber, 30 phr of high-cis polybutadiene (neodymium catalyzed) and 50 phr of N220 carbon black as a filler is crosslinked with sulfur.





The natural rubber SVR10², which is frequently used in practice, was used in the reference compound while the natural rubber component in the second testing compound was substituted with BISIKA rubber. The components were mixed in two stages, with the base compound containing the filler prepared first. In the second mixing step, the sulfur-based crosslinking system was added to generate the final vulcanizable mix. The vulcanization kinetics of both finished compounds was determined at different temperatures (150, 160 and 175 °C). The BISIKA system was found to cross-link somewhat more slowly, i.e. the vulcanization times (t₉₀) were consistently about 30 percent longer than for the mixture with the natural rubber SVR10.

The production of test tires

The test tires were manufactured by the renowned German tire retreader King Meiler³. King Meiler has been manufacturing tires for passenger cars, light trucks, SUVs (4 x 4) and racing cars for 60 years. Well-known rubber manufacturers have worked with this company for many years on the development/optimization of their synthetic rubbers. The main advantage of using retreaded tires for tire testing is that recycled carcasses can be used and only the actual tread material needs to be provided.

The demonstrator tires were manufactured using hot vulcanization. Here, the vulcanizable ready-to-use compound >

LAT100 measurements and external project facilitators

External project facilitators from industry and research are brought in as advisors for internal projects of the Fraunhofer-Gesellschaft in order to provide additional expertise and perspectives.

We would like to take this opportunity to thank Dr. Roland Krafczyk (Evonik Resource Efficiency GmbH), Prof. Gerrit A. Luinstra (Universität Hamburg) and Dr. Dirk Ruppelt (Gezolan AG) for the constructive discussions as well as the many technical tips and suggestions they provided in the course of the BISIKA project.

Through the support of the project facilitators, Fraunhofer also had access to the LAT100-Test at Evonik Resource Efficiency GmbH. Dr. Michael Heinz – proven expert for this method and member of the DIN Standards Committee for Materials Testing – conducted testing on both tire tread compounds.

Results of the LAT100 test:

“In general, one can say that the ‘S42705 BISIKA’ compound is significantly better than the ‘S42705’ compound [natural rubber reference]. This potential is particularly evident at high speeds. This behavior compares to DIN abrasion.”

Dr. Michael Heinz
Evonik Resource Efficiency GmbH

is distributed evenly over the surface of the processed carcass by extrusion and pre-treated with a "rubber solution" to provide adhesion. In the next step, the unprofiled tire is placed with the finished compound in a heated molding press. The mold is closed and the profile is formed based on the contour of the molding press. The tread is vulcanized and firmly bonded to the carcass after a specific period of time and based on a defined temperature and pressure curve (> 150 °C). A hot vulcanization process was used to produce both tire types - the natural rubber reference tire and the BISOYKA tire. They had identical treads and uniform recycled carcasses (Michelin) with 205/55R16 91V Sport dimensions. The vulcanization process was adapted to the respective compounds based on the crosslinking kinetics. Two sets of four tires each were produced with treads made of natural rubber or BISOYKA rubber.

Tests: BISOYKA rubber surpasses natural rubber

The aim of producing demonstrator tires with treads made of BISOYKA rubber was to evaluate them under application-relevant conditions. The evaluation of the abrasion was of primary interest as it is generally very difficult to quantify in laboratory tests. The testing approaches for evaluating tire abrasion vary widely among testing labs.

Test report of the Prüflabor Nord testing lab:

**"The tires of the green class
(= BISOYKA) exhibited better results
in all aspects under evaluation."**

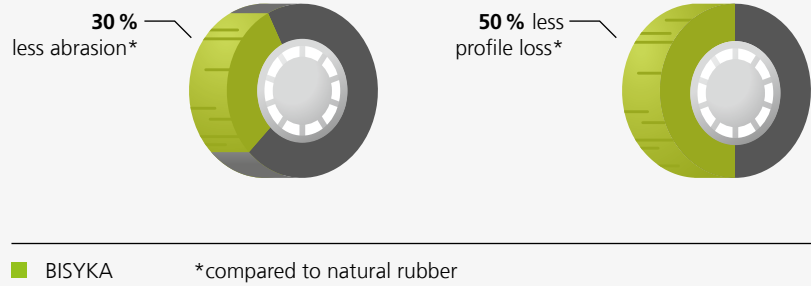
**Peter Kleingarn,
CEO of Prüflabor Nord**

After considering a wide range of test concepts, the BISOYKA consortium chose to carry out the tire tests at the Prüflabor Nord⁴ testing lab. Circuit tests were conducted to determine abrasion, while the rolling resistance was determined using a drum test rig. The grip parameters (wet and dry grip) were ascertained using measuring trailers in accordance with UN ECE 117. The circuit tests to determine abrasion were carried out at a speed of 25 km/h on a circular track with a diameter of 20 m. Two demonstrator tires of both compound types were mounted on standard 16 x 6.5 rims on the front axle of a Mercedes Benz Vito 116 (2.9 bars of air pressure, front wheel load of 550 kg). After a break-in distance of 100 km, the tires were visually reassessed and their air pressure was checked. The actual circuit tests alternated between 100 clockwise laps and 100 counterclockwise laps until a total number of 1,400 laps was reached. The distance travelled in the circular laps was just under 90 km.

The results of the comparative tire tests are summarized in the chart. The result: The BISOYKA tire outperformed the natural rubber-based reference tires in all aspects of the tire test conducted by the Prüflabor Nord testing lab. The rolling resistance was lower (one class) and wet and dry grip were marginally higher. Abrasion behavior – an important criterion for any natural rubber substitute – was significantly better than that of the retreaded natural rubber-based reference tire. The test report from the Prüflabor Nord⁵ testing lab came to the following conclusion: "The tires of the green class (= BISOYKA) exhibited better results in all aspects under evaluation."

The Fraunhofer BISOYKA project concluded on this successful note. However, it ends on the assumption that this is just the beginning of a long story! |

BISYKA rubber surpasses natural rubber



TEST RESULTS OF A COMPARATIVE TEST BETWEEN NATURAL RUBBER AND BISKYA TIRES

Performance characteristics	Reference 70 % NR, 30 % BR tires 18001 (red)	BISYKA 70 % BISYKA, 30 % BR tires 18002 (green)
Rolling resistance CR drum test rig	8,4 – Class C	7,6 – Class B
Dry grip DG measuring trailer	504 kg – Class C	525 kg – Class C
Wet grip WG measuring trailer	412 kg – Class C	426 kg – Class C
	Before the test: Tread depth: 7.30 mm Tire weight: 9,750 g	Before the test: Tread depth: 7.30 mm Tire weight: 9,550 g
Abrasion measurements AB circuits 1,400 laps	After the test: Tread depth: 6.36 mm Tire weight: 8,900 g Weight loss: 850 g Tread loss: 0.94 mm	After the test: Tread depth: 6.38 mm Tire weight: 8,950 g Weight loss: 600 g Tread loss: 0.47 mm

SUMMARY AND OUTLOOK

Summary

The BISOYKA project has succeeded in producing a nature-identical, biomimetic synthetic rubber. Initial practical tests with the BISOYKA tire compound have shown that there is about a 30 to 50 percent reduction in abrasion compared to natural rubber tires. This innovation was made possible by effectively combining the Fraunhofer-Gesellschaft's expertise in the fields of elastomers, biosciences and silicate research. BISOYKA rubber can also be produced on a technical scale in existing rubber synthesis plants without requiring much modification.

OUTLOOK

Know-how for the elastomer industry

The work carried out so far is, first and foremost, a starting point, as there is still a great need for development and optimization – for example in the field of composites. The know-how gained by the project is already being used to effectively address and solve customer-specific problems.

Material development and assessment of truck tires

The truck tire market, which is of interest for natural rubber and thus also for BISOYKA rubber, is large. In Germany alone, around 6 million tires are sold every year. In addition to new products, the increasing number of retreaded tires is also of interest, as biomimetic rubber is mainly aimed at being used for the treads. For Fraunhofer, this opens up a large R&D market potential. Experience has shown that two-thirds of the research activities are generated in the area of materials development and one-third in the field of analysis.

Anti-allergenic latex products

Another extremely interesting field of research is anti-allergenic latex products. BISOYKA rubber can significantly reduce the number and content of biocomponents, thereby avoiding critical protein structures. At the same time, the typical

properties of natural rubber are retained. This will make it possible to achieve a breakthrough in this high-priced market segment with regard to sensitive and, at the same time, effective and safe elastomer products.

Fraunhofer as an interface between rubber manufacturers and elastomer end products

A continuation of the highly successful cooperation between the five Fraunhofer Institutes offers the unique opportunity to be positioned at the "information-critical" interface between rubber manufacturers and producers of elastomer end products. The Fraunhofer constellation, which spans multiple areas of research, makes it possible to avoid unnecessary frictional losses in R&D, to combine new findings from both "worlds" and thus to advance material developments quickly and efficiently.

Isoprene from renewable raw materials

One ecologically feasible approach is to use renewable raw materials to produce the isoprene used in the BISOYKA. Together with other partners, Fraunhofer is currently investigating the possibility of developing a cost-effective and sustainable process. |



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