VIRTUAL 
EDUCATION IN 
RUBBER 
TECHNOLOGY 

SUMMARIES 
2007
VERT

A professional training program for the rubber industry called Virtual Education in Rubber Technology (VERT) has been developed by different European universities and companies:

- Tampere University of Technology, Finland
- Nokian Tyres Plc., Finland
- University of Twente, the Netherlands
- HAN University, the Netherlands
- Läroverket AB, Sweden
- Alexander Dubcek University, Slovak Republic
- Matador Rubber s.r.o., Slovak Republic

This work is supported by the EU within the Leonardo da Vinci program.

The VERT training program is a unique in the sense that it presents an educational program covering the full knowledge on components, design and production of rubber products up to the assessment of the performance of the rubber end-products (e.g. tyres) as part of a complete systems (e.g. vehicles) for the first time. It is a flexible program in the sense that an individual choice of the relevant parts of the training material can be made.

The program contains following modules:

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This is the first course in the VERT program. Orientation to web-based learning advices successful way to study on the web.

**Web-based learning - Why and What?**

Web-based learning is one way to learn, using web-based technologies or tools in a learning process. It consists of technology that supports traditional classroom training and online learning environments. "Pure" web-based courses are wholly based on computer and online possibilities. In this case all the communication and learning activities are done online. On the other hand, web-based courses may have some face-to-face sessions as well besides the distant learning tasks.

Web-based learning and traditional learning are similar in terms of desired goals: **to acquire new knowledge and skills.** In both ways the teacher is mentoring and students are doing various learning activities. The biggest difference between web-based learning and traditional learning is in **communication issues.** Web-based learning offers many opportunities for interaction with both students and instructors. In a traditional way of learning communication and interaction take place mostly at the same time and place as face-to-face meetings.

Due to the distance between the teacher and students in a web-based learning **new learning and teaching approaches** are needed. Web-based learning enables **learner-centred approach.** The main idea behind teaching is to guide and facilitate learning. Group work and independent learning are at the same time the key words of web-based learning. In traditional learning **teacher-centred approach** is more common, teacher giving/providing knowledge and students passively receiving it.

As a result from new teaching and learning approaches **student assessment** in web-based courses is also different. In a classroom setting it is usual to have an oral or written exam after the course. Most popular ways to assess students in web-based learning are:
• discussion forums, where teacher can observe the student's active participation;
• online multiple choice test, where you can do (self)test;
• e-portfolio, where you have collected all your material and assignments electronically during the course;
• report or essay, where you can analyse and express your comprehension based on the content of the course.

How do we learn?

We all learn in different ways. Some of us learn well by working in groups, discussing and sharing ideas. Others learn better by listening music or reading silently in the library. Differences are due to our experiences, habits and personal innate ability to learn. We all have our own particular way of acquiring new information - this is called a learning style.

You can find many ways to divide learning styles in educational literature. The simplest way is based on human's senses: visual - memory of graphs, illustrations and text; auditory - remembers sounds, speeches; kinaesthetic - learns best from doing something by hands.

Based on the learning style you use certain learning strategies. Perhaps you have noticed that you like some learning situations more than others, such as you prefer group work instead of sitting silently in library and reading. This is called your personal learning strategy, your way to learn and organize material more effectively and efficiently.

Web-based learning is best suited to students who are:

• Independent learners able to learn without classroom activities, face-to-face interaction or constant guiding and directions from teachers;
• Familiar with computers and technology or at least willing to learn how to use them;
• Self-motivated, well organized in terms of time and structure of the course;
• Busy with their families or work, far from universities to be on campus.

Me as a Learner

It is essential to know about yourself as a learner, your capacity to learn, your successful learning strategies, dominant learning styles, your strong sides and disadvantages. Furthermore, level of motivation and interest with respect to learning activities are also important aspects in learning. In addition to aforementioned,
understanding the nature of learning process and being aware of it help a lot to be a successful learner.

**Study Methods on the Web**

Web-based learning may sound very attractive, as it is possible to study either home, at work or some other place with a computer and connection to the web, any time that suits you. However, this does not necessarily mean that studying is going to be any easier - the time you used to spend on lectures is needed for independent studies with learning material on the web, with various exercises, assignments and queries as well as for collaborative work with other students, for web-based discussions etc.

Web-based learning means, for a large part, working independently and alone, with a computer and books or some other written or visual material. However, it may also include communication and collaboration with the trainer, tutors and other students. Communication and collaboration on the web is somewhat different from face-to-face situations, so you will need to know some basic things about how to act on the web to make this kind of action successful. Every student has an influence on how well grouping and the feeling of being together with others are realised. Communication, as well as many of the exercises and assignments, requires writing skills and information literacy, so they are introduced as well.

**Communication on the Web**

While studying on the web, an important part of the study process is communication. Web-based discussions can be arranged for many reasons and purposes and they can develop your skills in many ways. Your teachers and tutors usually start the discussion and tell what the discussion is about and what its aims are. Discussions can be, e.g. changing opinions on some theme, argumentation or commenting.

Especially important is **not to become invisible** - active communication enhances your own learning. It also ensures you get the support you need at the right time. It may also be one of the things taken into consideration when you are given a mark for the course. So, if you know you won't be able to participate to common working for some reason tell your teacher and other students that.

**Collaborative working on the Web**

The web makes it possible to work in groups although participants are far away from each other. Collaborative work on the web gives you a chance to benefit from other students' know-how, as well as bring your knowledge to benefit the others.
There are some things to remember to make sure that collaborative working is successful. First, commonly set goals make working easier. This means also commonly set schedules for working. It is very important for the group's success that each member is committed to working together and follows these schedules and other agreements.

Second, each member of the group should be active not only in their tasks but other communication. Group discussions give a genuine possibility to express yourself, share opinions and learn from others.

**Citing - what, when and how?**

In many cases, writing essays and papers require you to read through other people's works and use them as starting points and references in your work. When you do this, you should remember to tell that to your readers. Everybody has copyright to his own work - even other students.

So, whenever you use other people's ideas in your work let your reader know that. This also helps your readers to find the material you have used, for example in case they find it very interesting. Appropriate citing and references are also indicators to your teacher that you have studied and absorbed what you were supposed to.

**The fine art of finding information**

There is an abundance of various search engines, directories and databases in the web, not to mention the plethora of materials it is possible to find with them. You don't have to and you absolutely shouldn't just settle for Google, although it offers a simple and straightforward tool to start to look for information.

Information seeking and retrieving is a process including the following steps:

1. Defining what kind of information you need and for what purpose:
2. Deciding on the right source for the information needed:
3. Retrieving information in an efficient way:
4. Choosing the right information from the results:
5. Using the information found

Evaluation of the material found on the web is somewhat different from evaluating printed material. Publishing on the Internet is very easy for anyone, so you should be careful about what material to trust and how to make the decision that the material found is appropriate to the intended use.

When you have found something you intend to use in your work, it is wise to write down the details of its URL and the date you read it in the web. The web is a changing
environment, and the place of the page as well as its content may change whenever. This is why it might also be a good idea to take paper prints of the material.

**My Study Plan**

**Planning is critical for any activity.** Good planning helps you to ensure that changes happen in the way you want them to. By carefully planning your study activities you will be more effective and successful in a learning process. A well-designed study plan helps you to follow the learning process and determine what you want to learn.

Before starting to develop a **personal learning plan** you should know the basic concept of learning process in order to be able to plan your learning in an efficient way.

Learning can be efficient if you understand your way of learning and learning process. You are also conscious what steps you should follow and what aspects and activities you should pay more attention to while learning.

Some specific skills are especially important in effective learning:

- ability to be initiative in learning
- ability to set up goals
- ability to manage time
- ability to be reflective to your activities
- ability to plan, select and analyse your learning strategies with respect to the task and assignments
- ability to be responsible in what you are doing
- ability to notice and correct your own mistakes
- ability to change and adapt appropriate learning behaviours and strategies when necessary
- ability to transfer your knowledge to another situation.

In addition to the knowledge about learning process, you also need to know yourself as a learner to be able to develop a working study plan that takes into consideration your weaknesses and strengths. **SWOT analysis** helps you to focus on your strengths and weaknesses as well as opportunities and threats. Although SWOT analysis is widely used in business, it is adoptable and suitable for other fields as well.

When adapted to learning, **SWOT analysis provides direction for minimizing your weaknesses and maximizing your strengths in a learning process**. Based on the analysis you can come up with successful strategic approach for improving your study
plan and learning. To analyze yourself from different point of views is not a simple task and it is important to be modest as well as realistic.
Orienting courses
Virtual Education in Rubber Technology (VERT), FI-04-B-F-PP-160531

SUMMARY
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Introduction
A modern, competitive firm has many requirements. It has to recognize the critical success factors, which are different for various kinds of firms.

The rubber industry does not essentially differ from other industrial branches. That is why the requirements for the personnel working in that special field of market are the same as in other industries, i.e. all workers need to be aware of new information and development trends, at least in their special fields of expertise.

Management and administration
Management and leadership are the key points of organization's administration. Management means profitable leading of business. It directs, how things should be done. Leadership means leading of people. It tells, what right things to do are.

The tasks of managers /5/
Strategy of the firm

The strategy of an organization is the direction and scope of an organization over the long term. It helps the organization to react to changing environment, to meet the needs of markets and to fulfill stakeholders' expectations. The main purpose of strategy is to gain advantage towards the competitions. Strategic decisions are also likely to demand an integrated approach to managing the organization.

Quality systems

Quality is one of the most important success factors in organization. That's why it has to be seriously taken into account in management. The term 'quality system' stands for the system that is used for realising and developing the quality. Systems have been developed to ensure and to ease the quality management of the organization. With the help of the quality system the strategies and the plans of the managements are also told to the whole organization. The quality system defines the organization, responsibilities, proceeding instructions, processes and resources needed (see figure below).

Elements of quality systems. A = act, P = plan, D = do and C = check.

Research and product development

Product development is one of the key functions in any commercial company. The company needs products, which can be produced and sold successfully. The firm can have different kinds of approaches in the development activities:
• R & D – Research and Development is a common term in large firms, for example automobile industry, airspace industry, pharmaceutical industry etc. R&D is a driving force behind economic growth, job creation, innovation of new products and increasing quality of products in general, as well as improvements in healthcare and environmental protection.

• Design is the term used by the consumer goods industry and it has an artistic image. The clothing industry e.g. uses the word as a term for creating new collections.

• Product development (often combined with R&D) is often used for comprehensive technically oriented processes. Developing home appliances, machinery and why not rubber and tyre industry belong to these groups.

  The objective of product development is to improve competitiveness through new innovations and to convert design ideas into commercial products.

The product development process can target on creating a totally new product or on modifying an existing product. The development project for a totally new products is much more comprehensive than a modification. A new product might mean that besides the product design, the whole production line must be designed.

New product ideas are created by various means. Intuition can be one base for them. The product development team is aware of a need in the market and innovates a product to satisfy that need. Or a proper market research may be carried out and on the basis of the study products are developed. Basic research may also be a source for product ideas. Different sources of ideas are listed in the attached picture.

The majority of ideas will never be developed into products, as they would not have been commercially successful. Therefore the product development process must contain several points of review, where ideas are analyzed and only the best ones will be taken further.

**Success in product development**

In product development, customers' demands have to be taken into account, so that the product will be profitable also in the future.

Product development is easy if the product range is only re-designed for the current market. But if totally new products are to be developed and sold to totally new markets, the success is more difficult to achieve. The dependences and connections between technology and market issues are listed in the enclosed table.
The connections between technology and market issues.

Areas of R&D in rubber industries

Research and development in rubber industries can be divided into the following fields:

- Raw material producers
- New and modified elastomers, including TPEs
- New fillers
- Additive development
- Curing systems
Product development areas:

- Industrial rubber product development
- New functional products
- Smart products
- Hybrid products including components made of different materials
- New production methods
- Machinery and mould developments

**Production**

Production is a combination of all functions that are needed to create products or services. The main tasks of production are to produce and deliver products in certain periods and amounts. Sufficient quality with minimum costs is the requirements in production. The different factors influencing production and logistics are shown in the figure below.

The production process of rubber products include the following phases:

- Raw material handling
- Mixing
- Component production
- Assembly
- Vulcanizing
Logistics

The significance of logistics has grown substantially in the last decade. European Logistics Association has defined logistics as: "The organization, planning, control and executing of goods flow from development and purchasing, through production and distribution, to the final customer in order to satisfy the requirements of the market at minimum costs and minimum capital use." Logistics is the controlling and planning of material flows so that the needs of the final customer are satisfied. The minimizing of expenses and capital spending is also important when material flow is followed through.

Basic principles of the logistic system

- System can fulfill the customers' needs
  - Short lead-time from order to delivery
  - Reliable deliveries
  - Good availability
  - No shipping errors
- Integrated stock management
  - All warehouses under one ADP (automatic data processing) control
- Cost effectiveness
  - Distribution structure
  - Running of operations
- Direct and fast market information from consumers
  - Fast response
  - System is supporting the strategic goals of increasing volume and market share
Quality

The meaning of the quality has changed during the years. Before the good quality meant that the product was flawless. Nowadays, it means developing of company. The aims of the good quality are:

- happy customers
- profitable trading
- safekeeping and growing competitiveness

The quality is an important part of employees work. The following points influence the quality of a company's products and factors contributing to it:

- **The employees of a company** achieve quality by ensuring their performance as good and as reproducible as possible.
- **The continuous training and educational level** of the company's staff are important.
- **Research and development.** Their purpose is to develop products with inherent quality, to make products that are technically good and perceived as high quality by the customers.
- **Production.** In quality terms, the best production manufactures products corresponding to the given specifications using methods as robust as possible. The process window of the product should be as large as possible.

Typical of the quality control procedures applied to raw materials of polymer products is:

- It can always be ensured that the supplied material conforms to the order
- Usually the raw material manufacturer characterizes his product and submits the specification with the raw material. In many cases the user relies solely on this specification.
- The analysis of polymers usually requires expensive equipment, high level of expertise, and a lot of time.
- An important point in the management of raw material quality is that only reliable sources are used.
- The higher the quality requirements of the final product, the more important the quality assurance of raw materials.
Quality control

The control of the manufacturing of high quality rubber products is a sum of numerous control factors. For instance, the production organization has to know and control:

- Compounds and their mixing
- Handling of reinforcing materials
- Rubber processing systems, i.e.
  - Fabrication of different components
  - Molding techniques
  - Milling, calandering, extrusion and assembly
  - Vulcanization
- Power transmission, compressed air, hydraulics, heating and cooling facilities, temperature and pressure control
- Energy conservation
- Material reuse
- The special features and techniques linked to the very products of the manufacturing firm

The production process is controlled on an on-going basis to ensure that the quality level stays constant. Information is gathered and documented at the various process stages to allow the monitoring of changes and deviations.

Products are inspected visually, and each product type is subjected to testing. The scope of testing and the method used shall comply with the product specifications.

Marketing and sales

Marketing is an important function in organization's strategy. The main tasks are:

- Scanning of demands
- Influencing demands
- Satisfying demands

Competitive methods of marketing (4P):

- Products and services that correspond to requests of customers
- Price, the right setting
- Place, availability
Promotion, giving information

The combination of the methods determines the success of marketing. The marketing mix is selected based on the product.

Ansoff has defined four alternative strategies for growth. The first is market penetration, which means that by aggressive sales and promotion it is possible to increase the market share with present products at the present market. The second is market development, where growth is achieved by selling the present products to new markets. New products are developed for the present market is the third. And finally a company can grow by diversifying to new markets with new products.

**Marketing strategies**

A company can select different marketing strategies, such as:

- **Non-differentiated strategy**: Similar products are offered to everybody. Production oriented approach. Good for basic products.
- **Differentiated strategy**: Modified products are offered to different segments, different labels for example. Good for large firms.
- **Concentrated strategy**: One segment is selected and all efforts are concentrated to that. Good for small companies.

**Brands**

- Branding is central to creating product or company identity. Product brand is always connected to a particular product or service. The consumer may not even know which is the company behind the brand. A company may also have several brands.

**Segmenting**

In order to describe and characterize a market, the total market can be divided into smaller segments. A segment must be defined so that its volume can be measured. It must not be too abstract and its consumers must fit into a similar pattern. Marketing is different for each segment.
**Cash Flow**

Financing of new product ventures must be planned in advance. At the beginning, there will be only costs. Product development costs are modest at the beginning, but when the project goes further, more and more costs will accumulate. Experimental marketing is often started before the product is ready, in order to launch it successfully. Only after sales starts some cash flow will be created. However, at the beginning more money is needed to cover the costs, which means that the project has a negative cash flow. After the break-even point this cash flow will turn positive.

**Market Planning**

Analysis of the current situation is the starting point for the marketing planning. History of sales, and total consumption per market and market segment must be calculated. In this way one can estimate the market share. Consumer attitudes and buying behavior may have to be studied by a consumer research. This usually clarifies the positioning in the market especially in comparison to the competitors.

A marketing plan includes target settings for sales volume and market share. Objectives for margins and productivity are also set. Change in the market positioning or improvement of the company and brand image may also be part of the targets.

**Retail Planning**

A retail company is much more visible to consumers than the manufacturing companies. Therefore a marketing planning project at retail level is a comprehensive project involving shop location, defining consumer target groups, positioning strategy, communication strategy and design of product range shop interiors and the total outlook.

Retail planning is started by analyzing the market place in terms of consumer behaviour and attitudes, needs and competitor situation. Opportunities are assessed by focusing on selected consumer groups with consumer studies if needed. A visual audit of current shops is carried out both for own shops and competitors' shops.

A retail strategy is formulated by identifying and by positioning the targeted consumer groups. Communication strategy and design strategy are created accordingly. The whole marketing concept is designed according to these targets, including shop interiors, environments, fixtures, colors, materials and lighting. The purpose is to achieve correct retail identity. After review of the concept, implementation starts. All fixtures, graphics etc. are purchased and installed.
**Summary**

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**Basic terms in Organic Chemistry**, Most important reactions of alkanes are: cracking (at high temperatures), substitution radical reactions - $S_R$ and radical reactions realized at high temperature, or under UV irradiation,

**Alkenes, dienes, alkynes** – structure, reactivity, addition reactions, Markovnikov’s rule. Industrial using of unsaturated compounds for preparation of vinyl – and diene monomers. Typical reactions of alkenes are: addition, polymerization of alkenes that is most frequently catalyzed by peroxides – radical polymerization, styrene and butadiene are monomers used for the tyres production.

**Aromatic compounds** – structure and reactivity, orientation and reactivity in electrophilic substitution. The typical reaction of the benzene ring (electrophilic aromatic substitution $S_E$ realized on the presence of catalyst), electron donor substituents: activate and support the substitution on the *ortho* and *para* position, electron acceptor substituents: deactivate and support the substitution on the *meta* position.

**The alkyl halides** - nucleophilic substitution and elimination. Organometallic compounds, properties, synthesis. Grignard’s agents (organomagnesium compounds)

**Alcohols, phenols, ethers** – their structure, reactivity, reactions and using for preparation of monomers. The boiling temperature of alcohols increasing with the number of – OH groups. In addition to the previous reactions nucleophilic substitutions, eliminations and oxidations are typical for phenols. Typical reactions of alcohols are *Nucleophilic substitutions* $S_N$ reaction.

Hydroxy group (OH) is a strong nucleophil and also a strong base. At the same time it is not a good leaving group. In order to perform nucleophilic substitutions we have to decrease the strength of -OH group. It is done through protonation of the lone electron pair of oxygen atom that leads to creation of water which is weak nucleophil and a good leaving group.

Similarly to halogen derivatives nucleophilic substitutions of alcohols can be accomplished through two mechanisms $S_N 1$ and $S_N 2$. 
In the first stage of the mono-molecular mechanism $S_{N1}$ the carbocation appears just after protonation when C-O bond disappears. The alcohols that afford stable carbocations react with nucleophiles such as Br⁻ or CN⁻, etc.

The substitution $S_{N1}$ on tertiary alcohol 2-methylpropane-2-ol affords 2-brom-2-methylpropane. $S_{N2}$ reactions with strong acids (H₂SO₄, H₃PO₄) at higher temperatures (125°C) can result in an intermolecular dehydration of the alcohol affording ether.

Elimination reactions - dehydration. Dehydration reactions of alcohols afford alkenes. Mineral acids (H₂SO₄, H₃PO₄) are used as reagents.

Oxidation reactions of alcohols. The product depends on the type of the alcohol. 1° (primary) alcohols are oxidised to aldehydes and further to carboxyl acids. Oxidation reagents: KMnO₄, K₂Cr₂O₇, CrO₃, MnO₂, Ag₂O etc. 2° (secondary) alcohols are oxidised to ketones and 3° (tertiary) alcohols are do not react with oxidation reagents.

Phenols are derivative with OH groups on the benzene ring, Phenol is an important raw material for plastics, synthetic fibres, dyes and drugs. The hydroxy group of phenols has electron donor character (+M>-I), it directs the next substituent by electrophilic substitution reaction to ortho and para positions. By the reaction of phenol whit Br₂/FeBr₃ is formed mixture of o- and p- bromophenol.

Ethers can be regarded as di-substituted derivatives of water having the general formula R-O-R. R can be an alkyl or aryl. The oxygen atom of an ether can form a closed ring together with the carbon chain (cyclic ethers such as oxidant or 1,4-dioxane). Typical reaction is electrophilic substitutions (SE) or Friedel – Crafts alkylation, etc.

Nitroderivatives, basicity of amines, diazo- and coupling reactions.
The high polarity of the nitro group causes acidification of the hydrogen atoms in α-position in nitroalkanes. In fact, this is the only reaction of nitroalkanes that is used in practise. Aromatic nitrocompounds are more important in practise. According to the pH they are reduced to different products: from nitrobenzene in acidic pH is formed aniline, in basic pH azoxybenzene, azobenzene or hydrazo- benzene. In neutral condition are formed nitrozobenzene and fenylhydroxylamine.

Amines - chemical properties are determined by the presence of lone electron pair on nitrogen atom. Amines are basic. Their basicity increases with increasing of electron density on nitrogen (+I effect of the substituent). Tertiary amines are exception because in addition to the inductive effect spatial effects are also present. 
$\text{NH}_3 < 1^\circ < 2^\circ > 3^\circ$
**Aromatic amines** (anilines) are less basic than aliphatic amines. It is the result of involving the lone electron pair on nitrogen in conjugation with $\pi$-electrons of the aromatic ring (+$M$ effect of the amino group). Amines have the properties of a nucleophile. Their typical reactions are reactions with acids, yielding ammonium salts and reactions with electrophilic particles.

Amines, especially aromatic ones belong among the most important half-products in organic synthesis, mainly in production of dyes and drugs.

**Hexane-1,6-diamine** (hexamethylene diamine (HMDA)) is one of the most technologically important amines. Its copolymerisation with adipic acid yields polymer “Nylon 66”. Other amino compounds of strategic importance in organic synthesis are diazonium salts. They are prepared by the reaction of nitric acid with aromatic amines that is called diazotation.

**The diazonium salts** which are produced are not stable, but their water solutions are relatively stable. Diazonium salts give two types of reactions:

a) **substitutions**, when diazo group is substituted by other nucleophil

Through this reaction, we can prepare a lot of different substituted benzenes that are difficult to prepare in other ways. Some nucleophiles afford $S_N$ reaction without a catalyst ($H_2O$, $CH_3OH$, $KI$, $NaN_3$, $Na_2S_2$), others only in presence of salts containing $Cu^+$ ions ($Cl^-$, $Br^-$, $CN^-$, $KNO_2$, $SCN^-$) they are called **Sandmeyer reactions**.

b) **coupling reactions** - some diazonium salts react with phenols or substituted anilines yielding azo-compounds. These have technical importance as dyes for textile, paper etc. They are also used as analytical indicators (methylorange).

**Isocyanates** are compounds which contain one or more $-N=C=O$ groups in their molecules. Monoisocyanates are used for modification of synthetic and natural polymers. Diisocyanates are utilised for preparation of polyuretans - the polymers that are used for production of foam plastics, elastomers, fibres, glues and paints. Isocyanates are highly reactive compounds, reacted with alcohols yielding uretans as products, with amines yielding substituted urea, with carboxyl acids giving amides and with water produced amine. Aromatic diisocyanates are the most important. Their reaction with diols or polyols (polyhydroxy derivatives) yields polymers with uretan group involved in the chain.

**Nitriles** - contain the nitril group $-C\equiv N$. Low nitriles are liquids with a good (pleasant) scent and they are soluble in water. Acetonitril $CH_3CN$ is a perfect polar solvent. Hydrolysis and reduction of nitriles are their only reactions of practical importance. In presence of lithium aluminium hydride, nitriles are reduced to primary amines.
Acrylonitrile is basic compounds for production of PAN - polyacrylonitrile synthetic fibres.

**Aldehydes and ketones**. The high reactivity of aldehydes and ketones is related to the polarity of their carbonyl group which determines the tree main centres for most of their reactions. Nucleophilic additions will take place on the carbonyl group. As a nucleophiles agents reacted alcohols, water or HCN.

Carbonyl compound give aldol condensation and crotonic condensation reactions. The krotone condensation continue by the additions – eliminative mechanism.

Addition of primary amines leads to the preparation of imines and of secondary amines – to the preparation of enamines.

**The carboxylic acid and carboxylic acid derivatives.** The characteristic functional groups of carboxylic acids is COOH group. The reaction of valeric pentanoic acid with ammonia is nucleophilic substitution. From the various carboxylic acid such as CH₃COOH, CH₃O-COOH, CICH₂COOH and F-CH₂COOH, the last carboxylic acid is strongest.

**Acyl and aryl halides, anhydrides, esters, amides** – are functional derivatives of carboxylic acids. Formally they are derived from carboxylic acid by exchanging hydroxyl group for another monovalent group RCO-X. All of them include an acyl group.

If X= halogen the derivatives are called acyl halides, if X = OCOR they are acid anhydrides, if X = OR they are esters. If X = NH₂ (NR₂) they are amides.

Carboxylic acids derivatives also react in nucleophilic acyl substitutions which lead to mutual replacement of different groups. For example, hydrolysis of amides affords carboxylic acids, alcoholysis of anhydrides leads to formation of esters and amides are formed by aminolysis of chlorides of carboxylic acids.

Esters, halides and tertiary amides also yield typical nucleophilic addition reactions with organometallic compounds.

**Special reactions** of some derivatives of carboxylic acids are: **Hofmann elimination** of amides of carboxylic acids - preparation of amines.

**Basic terms in macromolecular chemistry**
Polymer is material composed of huge macromolecules. Since the beginning of life it exists in natural form, where e.g. nucleic acids, proteins or polysaccharides play main role in organism of animals and plants. Great number of polymeric materials, such as
plastics, elastomers, fibers, paints or adhesives that we come across in everyday life, is obtained synthetically. Dimensionally big macromolecules are produced from monomers during chemical reaction, when it comes to binding of monomers into chains. This phenomenon is known as polymerization.

**Properties of polymers in solid state and of amorphous polymers** - Linear polymers without regular stereoregular structure or other structural presumptions for, crystallization occurs in amorphous state. Polymer chains in this state are interlaced in polymer clusters with the chains of neighboring clusters. That means that clusters are mutually permeated. Characteristic for polymers in amorphous state is their behavior during transition from solid into liquid state.

**Crystalline State of Polymers.** Some polymers are totally amorphous at all events, other are partially crystalline. Polymer in crystalline state has molecules arranged in regular formations similar to crystal lattice. Important is also the influence of intermolecular interactions as for instance: dipole – dipole, hydrogen or ion bonds.

**Glassy, high elastic and plastic state**
Thermal motion in chains is changing along with temperature what reflected on polymer abilities. Polymer is hard and fragile at low temperatures. While energy is consumed only on vibration motion of atoms around their steady positions and chain is immobile as a whole, then the polymer is **in glassy state.**

Temperature scope characterizing transition period between glassy and rubberlike – elastic state is characterized by temperature of **glassy state** \( T_g \).

When thermal motion during another heating of polymer exceeds the interactions caused by adjacent binding forces then the molecules begin to mobile as a whole. In contrast to glassy state, the viscous deformation is of irreversible character and we call it **plastic state.** Temperature interval between rubberlike – elastic and plastic state is called **flow temperature** \( T_t \).

**Free - radical and ionic polymerization. Copolymerization.**
Radical polymerization belongs to the most important reactions running by chain mechanism. Mechanism of polymer chain creation can be described by elementary actions: initiation, propagation, termination and transfer reactions.

**Ionic polymerizations** have more complex mechanism than radical polymerization. They very often run with great speed even at temperatures deeply below \( 0^\circ C \), e.g. at \(-100^\circ C\). They differ from radical polymerizations not only by the way of initiation but also termination. Ionic polymerization is often realized in the presence of solvents that can participate on partial reactions and influence reaction speed and molar mass of incipient polymer.
**Block-, solution-, suspension- and emulsion polymerization**
There is only pure monomer with addition of initiator or catalyst present in the system during block polymerization. In the case of heterogeneous block polymerization, polymer is excluded from the monomer medium as the soft precipitate. Dilution of monomer with inert solvent considerably eases reaction heat dissipation. Polymerization then runs in solution. Solvent decreases viscosity and eases mixing of polymerization system.

Radical polymerization of monomers insoluble in water is often realized in water dispersion. Monomer along with initiator is dispersed in water in the presence of suspension stabilizer. Results of mixing of such a mixture are spherical drops of monomer with initiator surrounded by stabilizer. Suspension polymerization technique has great importance in practice. It is used for production of polyvinyl chloride, polystyrene, polymethyl methacrylate and also copolymers.

**Emulsion polymerization** belongs to radical polymerizations of monomers that are non-soluble or just slightly soluble in water. Polymer is obtained in the form of so-called latex, what is usually very stable soft dispersion of polymer in water. For some technological applications (e.g. paints) is latex the final product.

**Modification of polymers, crosslinking, stabilization, degradation of polymers.**
Production of chemical cross-links between linear macromolecules occurs during polymer cross-linking. Cross-links can be formed either during the process of polymer synthesis, or additionally by reaction leading to connection of already finished macromolecules. Cross-linked polymer could be also produced during chain polymerization, when there is cross-linking monomer present in polymerization system (for example divinylbenzene or glycol dimethacrylate containing two double bonds at styrene polymerization).

In the process of polymer degradation comes to disruption of macromolecule chains by the impact of physical (heat, mechanical stress, light, or other radiation) and chemical (oxidation and hydrolysis) influences (thermic degradation and chemical oxidations).

**Types of average molar masses, methods for determination of molar masses.**
Generally used methods for determination of average molar mass of polymers come from observation of some characteristic physical or chemical properties of their solutions. Molar mass of polymer can be expressed by its numeric or weight average. Methods leading to determination of numeric average of molar mass (\( \bar{M}_n \)) usually use observation of colligative properties of solutions. These methods are mostly membrane osmometry, ebullioscopy, or cryoscopy.
membrane osmometry - osmotic pressure measuring is the most sensitive of all methods used for measuring of solvent activity. For osmotic pressure of diluted solution of small molecules holds that \( \pi = RT.c / M \), where \( M \) is molar mass of dissolved substance, \( c \) is solution concentration, \( T \) is absolute temperature and \( R \) is gas constant.

Cryoscopy and ebullioscopy - both methods for determination of molar mass numeric average are derived from well-known Clausius-Clapeyron equation. On the basis of this equation, we can determine average molar mass of polymer from decrease of solvent’s congealing point \( \Delta T \) (at cryoscopy) or increase of solvent’s boiling point \( \Delta T \) (at ebullioscopy). Use of both methods is thus limited to characterization of polymer with low \( \bar{M}_n \) - to 30 thousands.

Light dispersion or sedimentation in gravitational field of ultra-centrifuge is commonly used for determination of weigh average of molar mass ( \( \bar{M}_w \) ). These are mostly absolute methods by which we can determine molar mass directly from observations of certain physical or chemical parameter. Regarding relative methods of determination, dependence between observed parameter and molar mass has to be calibrated by absolute method. Such method is, for instance, viscosimetric determination of polymers’ molar mass.
Rubber Physics
Virtual Education in Rubber Technology (VERT), FI-04-B-F-PP-160531

SUMMARY

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Continuing education has become a priority of every modern society which wants to maintain progressive development trends and to develop continually. Nowadays, technical advance depends on constantly rising intellectual potential of a society that does not often have time to follow modern trends in technical innovations. Therefore it is necessary to look for effective ways of balancing this handicap.

Continuing education is an effective way of solving this problem and it concerns all employees, from the workmen categories to engineers and researchers.

This was the concept of a course called „Rubber Physics“ devided into seven chapters. The course originated in a creative interaction of university teachers from many European countries that have a lot of experience in this field. It has also created a framework for a discussion of experts from Eastern and Western Europe that were being developed more or less in an isolation in the past.

The course contains basic information from the field of material rubber engineering and polymer materials that the workers at all levels of production and technological processes in rubber industry should know to a certain extent. Like in the whole course, also in this part at the end of each chapter, there are simple questions that a reader can use to check their understanding of a text.

The course is prepared so that it does not demand much mathematics knowledge. On the other hand, to the largest degree it must describe individual physical phenomena that we can come across in the polymer physics. This way the course enables a reader without a university degree to understand the problems of physical processes existing in rubber and polymers. It is necessary to stress that the whole issue presented in the course has also been tested at a sample of students that communicated with a lecturer, which resulted in proving the minuses that occured during its formation.

Let’s aproach the characteristics of individual chapters from their content aspect. The first chapter is called Polymers structure and it deals with the basic information about various types of polymer chain-like structures being specified in terms of their possible structure “variations “ as well as of the energy view, especially cohesive energy. The attention is paid also to the polymer chain geometry, cis and trans structures, isotactic and
symbiotactic polymers. A listener gains some basic information this way about various types of polymer structures that the following chapters relate to.

The next part of the first chapter describes phase states of polymers with an emphasis on an amorphous phase formation as well as with knowledge from the crystalline material structure. Besides, there are also connections between a structure and mechanical properties of viscoelastic materials in the context of elastic and aelastic processes projected into the dependency - consistency versus temperature. So a reader can see the interdependency of the consistency of various structures and the temperature.

The reader will also get knowledge about the way the individual phases formation depends on the cooling speed. Basis of Cohen-Turnbull theory of perforate liquid model and Arheny relation are described here. The viscosity theory is analyzed historically through individual models presented by Vog, Fulcher, Tamman and also Williams-Landel-Ferry in connection with a glass transition. The so-called WLF /Wiliams Landel Ferry/ equation represents a constantly topical view of the polymers viscosity. In the other part of the first chapter, there is also analysed Gibbs and Di Marzi theory together with Simhu and Boyer theory about a molecular capacity. As a result, the listener will, in this chapter, gain an overview of the structure and phase properties of polymers and will be ready to study other parts presenting knowledge about structure influence on specific physical parameters.

The second chapter pays attention to polymers mechanical properties. It is based on the analogy of solid substances mechanical conduct that comes out of action of force between the individual atoms and it also describes particular forms of defects in crysytallic structure that are typical of metals. Basic concepts are defined, for example Hook law, not only for tension alias pressure deformation but also for sliding deformation. It also defines the concept of Poisson number nad designs a microscopic view of Young model of elasticity. In this context, there are tensor properties presented in the chapter that we can come accross when dealing with solid substances. The description of the mechanical properties of elastic and viscoelastic materials would not be complete without considering thermodynamic aspects of the deformation. This part describes basic thermodynamic parameters and their relation to the material mechanical properties.

In order to understand the rubber performance in an interaction with fillers, we have to explain the so-called Payn effect that, like Young or sliding modul, descends according to the increasing static or dynamic load. This topic is worked up in the third chapter which stresses that this specific performance of filled polymers results from the filler and matrix material interaction. The fillers like soot or SiO$_2$, that are also called silica, are used frequently nowadays in the process of tyre production and the production of rubber mixtures for these products. Understanding the structure mechanism of Payn effect influences to a large degree their lifespan as well as use properties.
In addition, this chapter focuses on viscosity description associated with a relevant mathematic apparatus. The reader will learn about the “reaction” of polymers and elastomers to a step applied load. The concept of a complex module is defined here, physical significance of its parts is described, with a stress on tangent of the loss angle as a feature which is used, apart from other things, to define adhesion in the wet and tyre rolling resistance.

With respect to practical applications of rubber mixtures mainly in the rubber industry, it is necessary to describe dynamic performance of rubber mixtures with regard to tangent delta depending on a frequency or a temperature. This can also be found in this chapter together with William-Lendl-Fery transformation allowing frequency temperature transformation.

The facts about viscose performance of materials from the view of their deformation would be incomplete if we did not describe the process from the quality or quantity frame of reference thermal viscosity dependency together with thermodynamic aspects of viscoelastic rubber performance similarly to our description of deformation using thermodynamic parameters found in the previous chapters.

In terms of rubber products lifespan, it is necessary to understand the breaches dispersing in rubber mixtures, which can also be found in the third chapter. Basic theoretical preconditions start from fracture mechanics and they are accompanied by pictures showing breaches dispersing in rubber mixtures.

In the fourth chapter we describe the details of Mäxvell and Voigt model (some literary works name it Kelvin-Voigh model) as well as their combinations together with pointing to the problems of electromechanical modeling of viscoelastic processes.

The fifth chapter deals with certain physical properties of polymer materials, where the reader comes across different, experimentally appointed dependencies for polymer materials, on basis of which the reader can make a picture of a specific performance of polymers in comparison with other, for example metal materials and have an idea about their possible applications.

The sixth chapter describes polymers electrical properties that play an important role in their practical applications. It also works with electrical conductivity of composite materials, with electric strength of polymer materials as well as with polymers dielectrical properties.

The last chapter (the seventh one) deals with physical processes influencing surface contact of two materials. We work here with hysteresis process and with a draft of individual theories describing hysteresis that is specific for plastic and elastomer deformation. The theories are discussed from the historic as well as from the content.
point of view. In this chapter, we pay attention to pasting and adhesion as well as to seeing adhesion as a surface problem.

Because rubber and polymers are under dynamically variable load during their practical application, we also analyse the problems of adhesion during a dynamic contact of two materials in terms of various theories that are described in this part.

Friction is a very important element of this chapter and it is defined in the historical context of various authors opinions about this topic. Friction is also analysed as a dynamic problem of a contact of two entities. This matter is accompanied by a number of experimental measurements of different materials being brought in contact and the friction in between them was measured.

We believe that the course Rubber Physics will be a useful education tool in the presented form for the workers in rubber industry and it will bring new knowledge for its improvement during the following practical application.
Rubbers - elastomers - are polymeric materials characterised by their ability of reversible deformation due to external deforming forces. The rate of deformation depends on the structure and molar mass of the deformed rubber and on external conditions of the deformation. This characteristics, referred to as elastic and/or hyper elastic deformation, is entropic in nature. It results from the ability of rubber macromolecules to form a more organised state under influence of deforming forces, changing from the thermodynamically most advantageous shape of a statistic ball into a retracted form without any deformation of chemical bonds between atoms of the polymer chain or without deformation of their valence angles. The reduction in entropy (\(\Delta S\)) with an unchanged free energy of the system (\(\Delta G = \Delta H - T\Delta S = 0\)) must be combined with a reduction in its enthalpy (\(\Delta H\)), what will be manifested externally by heating the deformed sample. Ideally, the macromolecules can restore their initial position once the deforming forces are removed and the sample will be cooled down to the initial temperature.

Rubbers usually have long and regular macromolecule chains without bulk substitutes with spatially oriented structural units. This is the reason why their segments are movable and able to rotate around simple chemical bonds even at low temperatures, as it can be seen in their low vitrification temperature Tg. Typical examples of such rubbers are poly-cis-1.4-butadiene and natural rubber (poly-cis-1,4-isopren), with Tg approximately –110 and –70 °C respectively. Tg increases with increasing irregularities in the polymer chain (trans-1.4 or 1.2 structural units in polybutadiene) or in presence of bulky substitutes (butadiene-styrene rubbers). Rubbers are solid polymers similar to plastomers below the vitrification temperature or crystallisation temperature (if the rubber can be crystallised). When heated, rubbers change their elastic and/or hyper elastic state to a visco-elastic state; and they become plastic and flow above the softening temperature (Tm). It is advantageous if rubbers crystallise at normal temperature only when subjected to voltage and their Tg is significantly lower that the temperature they are used at.

Natural rubber comes from a plant. Synthetic rubbers are usually made by constructional polyreactions of chain-growth (radical and ionic polymerisation and copolymerisation, coordination polymerisation) or step-growth (polyaddition, polycondensation) nature. The type of polyreaction has a significant effect on their structure (microstructure, macrostructure, supramolecular structure), therefore on their processing and usage properties. In terms of their application and basic properties rubbers can be divided into:
Natural rubber (NR) is acquired from the Hevea Brasiliensis tree. The tree is grown in orchards in South-East Asia, Western Africa and northern parts of Southern America. The rubber obtained from the tree comes in the form of latex; a small part of it is processed directly. Rubber, poly-cis-1,4-isoprene (containing more than 99.9% of cis-1.4 structural units) is obtained by latex coagulation with mild acids. A part of non-rubber ingredients present in latex (5-10%) stays in the rubber influencing rubber properties and these ingredients are one of the reasons giving different properties to natural rubber and its synthetic equivalent (IR). NR always contains a gel. Natural rubber storage is accompanied by a progressive increase in its viscosity, which is externally manifested by hardening. NR shows very good elastic properties (Tg ~ -70°C) and spontaneously crystallises also under influence of deforming forces. It has excellent strength characteristics which are maintained also in the form of vulcanizates. It belongs to high resilient rubbers. It reacts with ozone and oxygen easily, therefore it has a low resistance to aging. Some commercial types of NR rubbers (with uncontrolled viscosity) must be plasticized before addition of additives. NR rubbers are usually cross-linked by sulphur system, but other cross-linking agents (phenol-formaldehyde resins, urethane, epoxy, fluorine rubbers and others) may be used, too.

Synthetic isoprene rubbers (IR) are made by anionic or coordination polymerisation of isoprene in a solution of non-polar aliphatic hydrocarbons. In addition to cis-1.4 structural units, macromolecules of these rubbers contain also trans-1.4, or 1.2 or 3.4 units. Li-IR (manufactured by anionic polymerisation) has a high molecular mass, very narrow distribution of molar masses and virtually linear macromolecules. Its crystallization is limited due to irregularities in arrangement of structural units. It has low strength and is quite difficult to process. Polymer molecules in Ti-IR (manufactured by coordination polymerisation) are branched with a relatively wide distribution of molar masses. Usually they contain about 15-20% of microgel. Their microstructure resembles NR, but they contain less cis-1.4 structural units than NR. Their workability is easier than in Li-IR and their properties resemble more NR than Li-IR. IR rubbers are vulcanized almost exclusively by sulphur vulcanization systems. With sulphur, they react more slowly than NR and their compounds show better safety of workability. They are non-polar, resilient, highly unsaturated. They have little resistance to oxidation and
Ozonisation, but they degrade more slowly than NR. Low building adhesiveness and permanency of form are typical for them.

**Butadiene** rubbers (BR) are manufactured by anionic or coordination polymerisation of butadiene, which can be found in polymeric macromolecules in the form of cis-1.4, trans-1.4 and 1.2 structural units. Content of specific forms depends on the polymerisation method and type of a catalyst used. These define basic BR properties. Tg of commercially manufactured BRs depends on proportions of different types of structural units in their macromolecules and it usually ranges from -100 to -80 °C. They are vulcanized by sulphur systems. Their reaction with sulphur is slower than the reaction of NR. No reversion usually occurs with over-vulcanization. BRs are non-polar, highly unsaturated rubbers. They are difficult to crystallise and they are easily subjected to cis-trans-isomerisation due to temperature. In addition to low strength, they are characterised by a high resistance to abrasion, high resiliency and good elastic properties at low temperatures. Their reaction with oxygen and ozone is slower than that of NR, but presence of anti-degradants in their compounds is essential.

**Butadiene-styrene** rubbers (SBR) belong to the most commonly used rubbers. They are copolymers of butadiene and styrene. Styrene and butadiene units may be arranged in statistical, partially block or block arrangements. Their properties are influenced not only by micro- and macro-structure of butadiene fragments in a copolymer macromolecule, but also by the styrene content. SBR does not crystallise even under voltage. The higher is the content of styrene and 1.2 structural units of butadiene, the higher is its Tg value. Block copolymers of butadiene and styrene can have even two Tg values (if they have a double-phase structure) and their values depend on representation of specific types of structure units in the blocks. At present, they are manufactured mainly by radical copolymerisation in emulsion (E-SBR) and by anionic copolymerisation in solution (L-SBR). E-SBRs have high molecular masses, broad distribution of molar masses, high degree of branching and they usually contain a gel. Their workability properties are good. The so-called oil extended rubber (OE-SBR) and their batches with carbon black are a special type of E-SBR. L-SBR have a narrow distribution of molar masses, they are practically linear and contain no gel. The are more difficult to work than E-SBR, but show better affinity to SiO₂. Their share in total SBR consumption continues to increase. Elastic properties of SBR deteriorate with higher styrene contents; these properties even disappear at high contents. The so-called styrene resins already show thermoplastic characteristics (containing more than 90% of styrene) and they are used only as active fillers or processing additives in rubber compounds. Similar to other unsaturated rubbers, SBR rubbers are vulcanised most frequently by sulphur systems. SBRs have very low strength, so active fillers are added to their compounds. The degradation rate of SBR rubbers and their vulcanizates is lower than in NR, but presence of antidegradants is still necessary.
Ethylene and propylene copolymers (EPM) and terpolymers of ethylene, propylene and a suitable diene (EPDM), most frequently of ethylidenenorbornene, rank among important special rubbers. EPM rubbers have no unsaturated bonds so they are very resistant to oxidation, ozonisation and several types of chemicals. EPDM rubbers have unsaturated bonds only in side groups, therefore the polymer backbone does not necessarily break during potential oxidation or ozonisation. Their content is low in commercial EPDMs (up to 10% by mass) and they usually disappear with vulcanization. Resistance to polar agents (diluted acids and bass) and to higher temperatures as well as excellent electrical insulation properties belong to important properties of ethylene rubbers and these properties are maintained also at elevated temperatures and in humid environments. EPMs are vulcanized by peroxide systems. In EPDM vulcanization, vulcanization systems typical for non-saturated rubbers are preferred, especially sulphur in combination with fast accelerators and ultra-accelerators, for resins and quinones. Both types of rubbers can be vulcanised by influence of irradiation. Elastic properties can be seen also in other ethylene copolymers (such as vinylacetate) and in chlorinated and chloro-sulphonated polyethylene.

Chloroprene rubbers (CR) belong to the oldest types of synthetic rubbers. They are manufactured by polymerisation of chloroprene in emulsion (G-CR, W-CR). They are highly polar, resistant to paraffinic and naphthenic oils, but they partially bud in aromatic solvents and degrade in contact with motor fuels; their flammability is very low and they show worse dielectric properties than non-polar rubbers. They crystallise to a high degree, so their strength is high with low permeability for gases and vapours. In comparison with other unsaturated rubbers, they have higher resistance to ozone and oxygen due to lower reactivity of the double bond. They are usually cross-linked by metal oxides (ZnO + MgO), but other cross-linking agents may be used, too, such as diamines, diphenols, thioketones or diazines.

Butadiene-acrylonitrile rubbers (NBR) are statistical copolymers of butadiene and acrylonitrile. Their special property is resistance to non-polar solvents, fats, oils and motor fuels that increases with higher content of acrylonitrile in the rubber. Their basic characteristics depend on the acrylonitrile content. The higher their content, the higher is their polarity, improving their resistance to budding in non-polar agents. However, their elastic properties and flexibility at low temperatures deteriorate, but their workability improves at the same time. Rubbers with 18-51% acrylonitrile content are the most common. NBR has low strength, limited resistance to oxidation and ozonisation and it is not suitable for applications at high temperatures. Semi-EV and EV systems are preferred for sulphur vulcanization, as they generate thermally more resistant vulcanizates; they can be cross-linked phenol-formaldehyde resins or peroxides. Hydrogenated butadiene-acrylonitrile rubber is characterised by higher resistance to higher temperatures and terpolymers of butadiene, acrylonitrile and acrylic acid or methacrylic acid have higher affinity to light fillers.
Acrylic rubber (ACMs) are polar rubbers showing a very good resistance to budding by non-polar oils, even by oils containing sulphur additives; they are also well resistant to higher temperatures, oxidation and ozonisation. Hydrolysis occurs in acidic environments. From chemical point of view, they are copolymers or terpolymers of various acrylic monomers or acrylic and non-acrylic monomers with functional groups suitable for cross-linking. Their elastic properties at low temperatures are influenced primarily by the structure of alkyl substituents in ester groups; they usually improve with the higher content of carbons in the alkyl substitute, however their polarity decreases reducing their resistance to non-polar oils and aging. At present, they are vulcanised most frequently by combinations of polyamines, higher fatty acids or their esters and by sulphur or sulphur donor. Efficiency of these systems can be improved by adding very fast accelerators or ultra-accelerators. Quaternary ammonium salts are used most often for cross-linking with the content of epoxy and carboxyl groups.

Isobutyl-isoprene rubbers (IIR) are special rubbers characterised by very low permeability to gases and vapours and with very good resistance to oxidation, ozonisation, thermal degradation and various chemicals. Isoprene is introduced into the polyisobutylene chain because of cross-linking and it has practically no effect on rubber properties, as its content in the copolymer is very low (0.5-6% mol). Sulphur-vulcanization of IIR and its co-vulcanization with other unsaturated rubbers is a slow process therefore fast accelerators and very fast accelerators and their combinations or systems based on sulphur donors are preferred. Quinone-dioximes and phenol-formaldehyde resins or their halogenated derivates are used in IIR vulcanization. Halogenated IIRs are more suitable for metal-vulcanization with diene rubbers. A developmental isobutylene-based types of rubbers are radial IIRs, which are easier to process, and bromide copolymers of isobutylene and p-methylstyrene, which are very resistant to ozonisation and high temperatures and reactive in co-vulcanization with general rubbers.

Special properties of fluor-carbon rubbers (FKM) are given mainly by their chemical structure. Polymer chains of these rubbers are saturated and made of structural units of various fluorinated hydrocarbons of ethylene and propylene types. The C-F bonds with high bonding energy (442 kJ.mol⁻¹) and low chemical activity are very important for properties of these rubbers. This is the reason why FKM have excellent resistance to effects of various chemical agents, including oxygen and ozone. They have high polarity, they are resistant against oils and motor fuels (also those containing methanol) and resistant against burning. They have the best resistance to high temperatures from among rubbers; they have very good resistance against hot oils, aliphatic aromatic and chlorinated hydrocarbons and concentrated acids, but they are not resistant to esters or ketones. The level of resistance increases with increasing fluorine content in their macromolecules. They can be cross-linked with diamines, peroxides and with fluorinated types of bisphenol A or organic tin compounds. Several developmental
types of fluor-carbon rubbers, such as fluortriazine, nitrose or fluor-alco-oxy-phosphazene rubbers find their application in rocket technology.

Epichlorhydrine rubbers (O) are special rubbers with saturated polymer backbone containing ether C–O–C bonds and chloro-methyl substitutes in the form of side branches. Polyepichlorhydrine CO is a polar polymer with a relatively high vitrification temperature Tg and low flexibility of polymer chains at low temperatures. Out of O rubbers, this rubber has the highest resistance to temperature and budding, very good resistance to burning and low permeability, also to motor fuels. Better elastic properties can be found in its copolymer with ethylene oxide ECO; however, it is less resistant to temperature and burning. The double bond in the side terpolymer group (ETER) is used for their cross-linking. Their properties resemble ECO rubbers. All the O rubbers are resistant to oxygen and ozone. Combinations with CO, ECO and ETER rubbers are often used in practical applications. Ethylenethiourea is often used for CO cross-linking; ETER rubbers can be cross-linked also by peroxides in presence of ethylenethiourea or sulphur.

Urethane rubbers (U) are manufactured by polyaddition reactions of diisocyanates and diols. Rubber-like properties can be found mainly in polyurethane-polyester (AU) and polyurethane-polyether (EU) copolymers. Their typical characteristics include primarily high strength, resistance to aging (they basically do not react with oxygen or ozone), to higher temperatures, excellent resistance of vulcanizates to abrasion, relatively good elastic properties at every strength level, low permeability of gases and vapours and relatively good resistance to budding in non-polar oils. Their disadvantage is a possible hydrolysis, especially in environments with hot water, vapour, acids and bases, even induced by lubricants, heat and extended effects of tropical climatic conditions. They are usually vulcanized by diisocyanates or peroxides in combination with trialkylcyanurate; they can be cross-linked even by sulphur if they have double bonds in their molecules.

The polymer backbone of silicone rubbers (Q) has no hydrocarbon nature. It is made of oxygen and silicone atoms with hydrocarbon substitutes linked to it - mostly methyl substitutes (MQ) or methyl ones combined with vinyl (VMQ) or phenyl substitutes (PMQ). Valence angles of Si-O-Si bonds in Q rubbers are bigger than valence angles in carbon or carbon-hydrogen bonds, so their polymer chains are flexible and elastic also at very low temperatures. Density of cohesion energy between macromolecules of Q rubbers is very low, what can be seen in their low viscosity and its minor change with temperature, with low strength and high permeability of gases and vapours. Q rubbers and their vulcanizates are extremely resistant to high temperatures; they usually withstand long-term temperatures of approx. 200 °C. They withstand intermittent temperatures of 300-400°C, however, in hot steam (120-140°C) they undergo hydrolysis and degrade. They are extremely well resistant to aging and ozone; they are even used in manufacture of hoses for ozone delivery. Qs have high adhesiveness, they are hydrophobic and physiologically compatible materials, so they are used as separation agents as well as implants and other materials accepted by human organisms.
Polysulphide rubbers (TM) and their vulcanizates are distinguished by their extreme resistance to budding in ketones, aromatic and halogenated hydrocarbons. In addition to this, they are very resistant to oxidation, ozonisation and UV radiation and they show low permeability for gases and vapours. Tiokol A is the oldest type of polysulphide rubbers. It is made by polycondensation of dichloroethylene and sodium sulphide. Also other types of dihalogenids, especially di-2-chloroethylformal and its combination with 1,2-dichloroethylene and also with 1,2,3- chloropropane (creating branched polymers), are used at present to produce polysulphide rubbers. Their elastic properties and partially their resistance to budding is given by the sulphur content. Selection of cross-linking agents depends on end group types. TMs with –SH end groups are cross-linked with oxidisers, such as p-quinone-dioxim, oxygen, cobalt salts or peroxides; TMs with -OH or halogen end groups are cross-linked with ZnO.

Thermoplastic rubbers (TPE, or TPR) are polymeric materials characterised by their elastic properties of vulcanizates and workability properties of thermoplasts. Such properties can be found in block copolymers made of elastic and plastic blocks, elastomer and plastomer compounds and in ionomer polymers. Unlike other rubbers, they have a double-phase structure in which the elastomer component makes up a united phase a matrix, and the plastomer component is dispersed in it in the form of domains. They maintain their morphologic structure also when deforming forces are applied. They are tough and fragile under the vitrification temperature of the elastomer matrix. They are elastic above this temperature and under the vitrification temperature of the polymer making up the domains, or below the crystallite melting temperature or associate breakdown temperature. Block copolymers of diene (butadiene, isoprene) and styrene belong to the oldest and most important thermoplastic rubbers. Most commercially manufactured styrene TPEs have their styrene content of about 20-30%. Polyester, polyurethane and polyamide TPEs are mostly multi-block copolymers with fairly short alternating elastic and plastic blocks. Out of polymer compounds of elastomer and plastomer nature, polyolefin-based compounds are used the most frequently in practical applications as thermoplastic rubbers. EPDM makes the elastomer phase, and propylene (PP), polyethylene (PE) or a compound thereof is a usual plastomer component. Similar to EPDM compounds, NR-based and polyolefin-based compounds have optimum properties if prepared by dynamic vulcanization, in which NR particles are moderately cross-linked. There are also oil-resistant thermoplastic materials (NBR+polyolefins) and thermoplastic materials characterised by low permeability for gases such as oxygen, nitrogen, water vapour, and for noise. Typical representatives of ionomer thermoplastic systems are zinc salts of sulfonated and maleinised EPDM with high ethylene content. Two types of thermolabile domains are found at normal temperature in morphologic structure of EPDMs modified in this way – crystalline ethylene domains and ionic associated made of polar groups of zinc sulfonic groups bound to the EPDM polymer backbone. Both types of the domains act as particles of an active filler and contribute to
improvement of EPDM strength characteristics up to the level of equivalent properties of its vulcanizates filled with active fillers.

Every rubber has the optimum properties in the form of vulcanizates. This is the reason why vulcanization is one of the most important processes in majority of rubber-making technologies. In this process, the plastic rubber mixture changes in consecutive and parallel transformation of its chemical and physical state to a final elastic product – a vulcanizate, rubber. Vulcanization is based on creation of chemical transverse bonds between rubber macromolecules resulting in a three-dimensional spatial mesh of a rubber matrix. The spatial mesh includes also physical links, such as hydrogen bridges, polar or dispersion forces between specific macromolecules and their various clusters created during the preparation or processing of the specific rubber compound. Other additives present in the rubber compound are chemically bound in the compound, dispersed or dissolved in it in their initial or alternated form. Various chemical-vulcanizing-agents are used to create the chemical transverse bonds between rubber macromolecules (such as sulphur, peroxides, metal oxides, resins, quinones and others), which can react with appropriate functional rubber groups in the process of vulcanization to create transverse bonds between them. The cross-linking can be induced also by various types of radiation emitting sufficient energy to generate reactive forms of rubber macromolecules - radicals in most cases. They react with each other giving rise to transverse bonds. Cross-linking can occur also due to microwave energy or ultrasound. Most rubbers require vulcanisation; though it is not inevitable for some type of thermoplastic rubbers.

Vulcanisation in presence of vulcanisation agents is basically divided formally into three stages. The first stage – induction period – involves an interaction of components of the vulcanisation system used; virtually no or very few transverse bonds are formed. Its duration depends mostly on the type of the vulcanization system and vulcanization temperature. In sulphur vulcanization, this is significantly affected by present vulcanization accelerators or retarders or scorching inhibitors. The second – main – stage of vulcanization involves the crucial vulcanization process – a fast cross-linking of rubber macromolecules and formation of the vulcanizate itself. The vulcanization rate can therefore refer to the rate of this stage. When the optimum vulcanization is reached, the created transverse bonds will be restructured and rubber chains will be modified in the third stage. This stage may be related to a reduction in the number of transverse bonds (reversion), what would be manifested in different properties of the final vulcanizate.

The number of transverse bonds to be created between the rubber macromolecules and their chemical structure depend primarily on content and activity of a vulcanization agent used and on temperature and time of vulcanization. The effects of temperature at which the vulcanization takes place can be seen mainly in the speed and these effects can be evaluated just like in other chemical reactions using the Arrhenius equation.
Firstly, the content of the transverse bonds increases non-linearly with vulcanization time and when the optimum is reached the content can even decrease (reversion). Properties of the vulcanized compound change at the same time with differing dependencies on the vulcanization time. Some vulcanizates properties achieve the optimum values even before the vulcanization optimum is reached. Vulcanizates properties and their tensile strength in rupture are directly dependent on their network density at low elongations, and/or to a reversed value of the average molar mass of rubber macromolecule segments found between two transverse bonds. Unlike in modules, in higher mesh density the vulcanizate’s tensile strength in rupture does not increase proportionally with the higher mesh density, but it decreases once it reached the optimum value. Specific values of vulcanizate strength characteristics depend also on other factors, especially on rubber structure and structure of transverse bonds. Vulcanizates based on synthetic rubbers have lower strengths than NR vulcanizates because they cannot crystallize due to various types of structural units (cis, trans, 1.4, 1.2,) or several co monomer units (e.g. butadiene, styrene, acrylonitrile and others) in their macromolecules. Similarly vulcanizates with prevailing polysulfide transverse bonds have higher tensile strength than vulcanizates with monosulfide or carbon transverse bonds. Relative elongation in rupture decreases at first with the higher mesh density, approaching asymptotically the minimum value. Vulcanizate hardness increases with vulcanization time just like their mesh density. A slightly under-cured vulcanizate has the highest structural strength; this property quickly decreases with time once the vulcanization optimum has been reached. The change in elasticity with increasing vulcanizate mesh density is similar to that in case of modules. It is directly proportional to mesh density and relative elongation in all three coordinates. When the vulcanization optimum is reached or when there are many transverse bonds between rubber macromolecules, it can get even lower with vulcanization time.

Rubbers, just like any other chemical compounds, can participate in other chemical reactions under suitable conditions (polymer-analogical reactions) such as cross linking. The basic prerequisite for participation in such processes is presence of suitable reactive function groups in their macromolecules. They are usually used to modify undesired properties of industrially manufactured rubbers (e.g. resistance to aging, polarity, adhesion to other materials, linkage of antidegradants), to introduce new function groups or to produce rubbers with some new properties (CIIR, BIIR, carboxyl rubbers). If the rate of change of the original function groups is low, typical properties of the rubber change only a little, but the rubber will acquire a new special feature. The higher the rate of change (20-30% or more), the higher is the probability that sine characteristic properties of the original rubber will change. For example, if a NBR rubber is selectively hydrogenated, it will maintain its resistance to budding in non-polar oils, but the higher the level of hydrogenation, the better his resistance to degradation and a NBR hydrogenated up to 100% conversion would be basically equivalent to FM rubbers in terms of resistance to aging.
A double bond is a characteristic function group in the most frequently used general rubbers. Their typical representatives are unsaturated diene monomer-based rubbers of both polymeric (e.g. NR, IR, BR, CR) and copolymeric (e.g. SBR, NBR) nature. Reactivity of double polydiene bonds in chemical reactions depends on their position in the macromolecule of the relevant rubber and on the type of substitutes found in the surrounding. In nucleophilic reactions, their reactivity is increased by nucleophilic substitutes and reduced by electrophilic substitutes. A good example of this influence is a significantly slower oxidation of a CR rubber compared to a NR or IR rubber. Similarly, nucleophilic structural units affect reactivity of the double bonds in 1.2 and 3.4 structural units of polydienes. The presence of the double bond in polydiene macromolecules is closely related to existence of reactive hydrogens in \( \alpha \)-position towards the bond, and these hydrogens are active in substitution reactions. The 4.1 bond connecting specific structural units is another reactive place. This bond is weakened due to a high energy of mesomerism, so it is easily decomposed to radicals. This occurs mostly in degradation reactions, specifically in case of mechanical stress applied on relevant rubbers. This happens most often at their potential plastification, in particular during preparation and processing of rubber compounds. Saturated rubbers are usually less reactive with low-molecular agents. Some of them even contain function groups whose chemical transition would be undesired, as it is usually related to deterioration of rubber properties. Hydrolysis of ester groups in acrylic rubbers in some types of polyurethane or polyester-based thermoplastic rubbers is a typical example.

Several types of intermediary reactions can occur simultaneously with the polymer-analogical reaction in chemical reactions of rubbers. In case of polydienes, this involves mainly cyclisation and cis-trans isomerisation and/or degradation or cross-linking.
Elastomeric Materials
Virtual Education in Rubber Technology (VERT), FI-04-B-F-PP-160531

SUMMARY

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Introduction to elastomeric materials

The natives of South America alighted on exploiting the latex of Hevea Brasiliensis rubber tree to produce waterproof footwear, among others, by soaking their feet to liquid, latex, tapped from tree. From the Indian word “caa-o-chu” (a weeping tree), inherit the words like caoutchouc in English and French, Kautschuk in German language, caucho in Spanish, caucciù in Italian. The word rubber originates from the early applications of rubber, i.e. from the property of caoutchouc to rub out pencil writing.

In the 18th century when rubber appeared in Europe it was used for the fabrication of suspenders and straps. Different kinds of materials were impregnated to be waterproof by rubber. However, the performance of the rubber articles was quite poor, because rubber was at that time still gummy and the fluctuation of temperatures caused great changes in products. It was only at year 1839 when Charles Goodyear conceived nearly by accident the vulcanisation of rubber, which made rubber as an elastic material capable of preserving its characters in large temperature range.

The idea of this part of “Professional Development Learning program for Rubber Industries” course is to give students an extensive view of the elastomeric materials. The structure and characters of most typical rubber and thermoplastic elastomers will be examined during this course. In addition, familiarizing with applications and testing of different elastomers, design and construction, as well as recycling of elastomeric products are to be handled.

Manufacturing process of rubbers

The manufacturing process of synthetic rubber starts by manufacturing of raw rubber. The first step in this process is polymerization. This is a chemical reaction, where small molecules (monomers) are joined together to form large molecules (polymers). Natural rubber is collected in polymerized form. So the manufacturing process of natural rubber
starts by mastication. Mastication is a process where molecules are physically or chemically shredded so that mixing and processing would be easier. This makes the rubber softer. Most synthetic rubbers do not need the mastication because they are made of shorter molecules. Peptizing agent prevents reactions between the broken chains.

Rubbers consist of elastomer and additives. Additives may be for instance fillers and vulcanisation agents. The purpose of additives is e.g. to improve properties or processability. Rubbers can be processed in many ways (e.g. compression moulding, injection moulding and extrusion). During the process or after that the rubber is vulcanised (cross-linked) when rubber elasticity and dimensional stability will appear. After the process and vulcanisation rubber product often has to finish by e.g. cutting.

**Behaviour of elastomers**

The predominant property of elastomers is the elastic recovery after deformation in compression or tension. Even after stretching of an elastomer many times its original length, it will return after removal of the tension under ideal circumstances to its original shape and length. In addition to this, elastomers are characterized by a great toughness under static or dynamic stresses, a better abrasion resistance than that of steel, by an impermeability to air and water, and in many cases, by a high resistance to swelling in solvents, and to attack by chemicals. Elastomers, like many other polymers, show viscoelastic properties, which nowadays can be tailored for numerous special applications, like e.g. tyres, vibration and shock isolation and damping. These properties are exhibited at wide temperature range, and are retained under various climatic conditions and in ozone-rich atmospheres.

Rubbers are also capable of adhering to most other materials, enabling different hybrid constructions. In combination with fibers, such as rayon, polyamide, polyester, glass, or steel-cord, the tensile strength is increased considerably with a reduction in extendibility. By joining elastomers with metals, components, which combine the elasticity of elastomers with the rigidity of metals, can be achieved.

The property profile, which can be obtained with elastomers depends mainly on the choice of the particular rubber, the compound composition, the production process, and the shape and design of the product. Depending on the type and amount of rubber chemicals and additives in a compound, vulcanizates with considerably different properties with respect to hardness, elasticity, or strength are yielded.

The viscoelasticity of elastomers and rubbers is easy to detect in practice. When stretching a cross-linked elastomeric band, rubber band, a temperature rise of the band can be observed as a consequence of emerging heat due to friction of viscous
deformation. The force that induces the recovery of deformed rubber, is dependent on the entropy of rubber material.

The temperature range of elastic behavior of elastomers is limited by glass transition temperature. At the temperatures lower than glass transition temperature the movement of molecule chains is very restricted, and the large elastic deformations are not possible. Elastomers are rigid and fragile materials under the glass transition temperature. The physical backgrounds of elastomeric behavior is described in more detail in the PDLRI section rubber physics.

**General properties of elastomers**

The property profiles of elastomers depend mainly on the choice of the particular rubber, the compound composition, the production process, and the shape and design of the product. Moreover, the character of loading e.g. whether it is static or dynamic, influences strongly in elastomer properties. Satisfactory properties can only be obtained by proper compounding of elastomers with chemicals and additives, and subsequent vulcanisation at adequate circumstances. Depending on the type and amount of rubber chemicals and additives in a compound, and depending on the degree of vulcanisation, a given rubber can yield vulcanizates with considerably different properties with respect to hardness, elasticity, or strength.

**Classification of elastomers**

Elastomers have been classified to groups according to similar properties and applications. Rubber types that have been standardized (ASTM D 2000, SFS 3551, SIS 162602) are suitable for several industrial applications (e.g. tyres, belts, tubes and seals).

**Rubber type 61 (rubbers for general use)**

Type 61 rubbers are used when the product does not require special properties, like oil, heat or weather resistance. These rubbers have good mechanical properties and processability. They also have low price. Elastomers that belong to this group are natural rubber (NR), polyisoprene rubber (IR) and styrene-butadiene rubbers (SBR) and the blends of these elastomers.

**Rubber type 62**

Rubber type 62 is rubber type that has not standard. Butyl rubber (IIR), chlorobutyl rubbers (CIIR) and bromobutyl rubbers (BIIR) are elastomers in this group. They have good ozone and weather resistance. In addition, the gas permeability is low and they are resistant to vegetable oils, but not mineral oils.
Rubber type 63

Rubbers in this group have good oil resistance, but ozone and weather resistance are weak. Applications are products that are touched with oils. Nitrile rubber (NBR) is rubber type 63.

Rubber type 631 is rubber that has developed from nitrile rubber. It has better ozone, weather and heat resistance than nitrile rubber. Hydrogenated nitrile rubber (HNBR) belongs to this group. Rubber type 632 is nitrile rubber blended with poly-vinyl-chloride (NBR/PVC). It has better oil, ozone and weather resistance than NBR.

Rubber type 64

Chloroprene rubber (CR) is representative of rubber type 64. It has good resistance to vegetable oils and pretty good aliphatic and naphtenic oils. Disadvantage is poor aromatic oil resistance.

Rubber type 65

Rubbers in this group have good weather and heat resistance and quite good oil resistance. Poly-acrylic rubbers (ACM) are in this group.

Rubber type 66

Rubber type 66 is not standardized. Polyurethane rubbers (AU, EU) belong to this group. These rubbers are tough and they have good weather and oil resistance. Heat resistance is poor.

Rubber type 67

In this group, rubbers (fluorocarbon rubbers (FPM)) have good weather, heat, oil and chemical resistance.

Rubber type 68

Silicone rubbers (Q) are in this group. They have good weather, cold and heat resistance. Mechanical properties are weak.

Rubber type 69

Epichlorohydrin rubbers (CO, ECO, GECO) belong to this group. They have medium weather, oil and heat resistance.
Rubber type 70

Rubber type 70 comprises ethylene-propylene rubbers (EPDM, EPM). They have good ozone, weather and heat resistance and poor oil resistance.

Other rubbers

These rubbers are not standardized:

- CM, chlorinated polyethylene (medium weather and heat resistance)
- CSM, chlorosulphonated polyethylene (good weather and acid resistance)
- EVA, ethylene-vinyl acetate copolymer (resistant to aliphatic oils)
- BR, butadiene rubber (good elasticity)
- XNBR, carboksylated nitrile-butadiene rubber (tough and oil resistant)

Rubber blends

Rubber materials in applications are always rubber blends. They contain basic elastomer or masterbatch and additives. This way the properties of material are improved or changed.

Compositions of rubber blends are described in recipes. The basic recipes are simple and they are standardized. These recipes can be modified when new blends are developed. Recipes inform the materials and amounts used in rubber blend. The amounts of constituents are usually represented parts per hundred parts of rubber (phr).

The basic recipe for rubber vulcanized with sulphur.

<table>
<thead>
<tr>
<th>Material</th>
<th>phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw rubber</td>
<td>100</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0-4</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2</td>
</tr>
<tr>
<td>Accelerator</td>
<td>0.5-3</td>
</tr>
<tr>
<td>Antioxidant</td>
<td>1-3</td>
</tr>
<tr>
<td>Filler</td>
<td>0-150</td>
</tr>
<tr>
<td>Plasticizer</td>
<td>0-150</td>
</tr>
<tr>
<td>Other additives</td>
<td>0-</td>
</tr>
</tbody>
</table>
Thermoplastic elastomers (TPE)

Thermoplastic elastomers are a polymer group, whose main properties are elasticity and easy processability. The use of thermoplastic elastomers has grown noticeably during a couple of last decades.

Thermoplastic elastomers are a wide material group. These materials have many advantages of which the most important ones are

- good properties in low temperatures
- excellent abrasion resistance
- damping properties
- good chemical resistance
- easy processability (compared to rubber)
- recyclable material

A restrictive features of thermoplastic elastomers compared to rubbers are the relatively low highest operating temperature (< 130 - 160°C), small selection of soft grades and high price of TPE's.

Thermoplastic elastomers are used in areas where elasticity in vast temperature range is required. The main applications are in automotive industry and sport accessories.

Thermoplastics elastomers can be divided in the following groups:

1. Styrene-diene block copolymer
2. Elastomeric alloys
3. Thermoplastic urethane elastomers
4. Thermoplastic ester-ether copolymers, TPE-E
5. Thermoplastic amide copolymer, TPE-A
Comparison of different TPEs

<table>
<thead>
<tr>
<th></th>
<th>TPE-S</th>
<th>TPE-V</th>
<th>TPE-U</th>
<th>TPE-E</th>
<th>TPE-A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density [g/cm³]</td>
<td>0,9-1,1</td>
<td>0,89-1</td>
<td>1,1-1,3</td>
<td>1,1-1,2</td>
<td></td>
</tr>
<tr>
<td>Hardness Shore A/D</td>
<td>30A-75D</td>
<td>60A-75D</td>
<td>60A-55D</td>
<td>40-72D</td>
<td>75-63A</td>
</tr>
<tr>
<td>Highest util. T. [°C]</td>
<td>70, 135</td>
<td>135</td>
<td>140</td>
<td>150</td>
<td>170</td>
</tr>
<tr>
<td>Compression set at 100°C</td>
<td>P(SBS)</td>
<td>F/G(SEBS)</td>
<td>P</td>
<td>F/G</td>
<td>F/G</td>
</tr>
<tr>
<td>Hydrocarbon resistance</td>
<td>F/E</td>
<td>G/E</td>
<td>F/E</td>
<td>G/E</td>
<td>G/E</td>
</tr>
<tr>
<td>Hydrolysis resistance</td>
<td>G/E</td>
<td>G/E</td>
<td>F/G</td>
<td>P/G</td>
<td>F/G</td>
</tr>
<tr>
<td>Price order [€/kg]</td>
<td>2...5</td>
<td>3...6</td>
<td>4...7</td>
<td>6...8</td>
<td>7...10</td>
</tr>
</tbody>
</table>

Processing

The processing of rubbers starts by blending elastomers and additives. After that rubbers are processed and rubber product is vulcanized so that the mechanical properties and the dimensional stability will appear.

The general characteristics of the processing methods of thermoplastic elastomer and thermoplastics remind each others. The most significant differences between TPs and TPEs lie in the values of processing temperatures and viscosity. In the case of thermoplastics the processing temperatures are usually higher and viscosity values are slightly lower than those of TPEs.. The most common processing methods of thermoplastic elastomers are injection molding, extrusion and blow molding techniques. The viscosity of TPEs is significantly lower than the viscosities of traditional rubber elastomers, which offers many processing advantage for TPEs compared with rubbers.

Design of elastomeric products

The purpose of design is to assist in converting inventions into successful innovations. The target can also be to prolong the life of a product by giving it a new outlook or shape (see also orienting studies product development and design )
The manufacturer of elastomer products can design the product at customer's specific request or develop new product and supply it for several customers. Technical rubber products are often developed accordingly the request of the customer. Tyre is a good example of the product that is designed by manufacturer and then marketed for customers. The product design is often made in co-ordination with customer. Elastomer component is often a part of bigger unit, which may include metal mountings, restrictions for size and form.

It is important that product meets requirements of customers better than products of competitors. It is also useful if product is suited to further development.

**Aspects cater to design**

- Elastomer type
- Dimensioning
- Shaping
- Economic efficiency of materials and processing
- Processing method
- Reinforcement

**Design process**

Theoretically the phases of design process are:

1. Defining the problem and needs for product development and outlining the project
2. Product development phase: Search for ideas and pulling them together to a concentrated solution, developing a prototype and freezing the design
3. Before deliveries, product sketches and data, modification of operating system, testing, full-scale production

**Elastomer selection**

The most important criteria of choosing elastomer:

- Flexibility
- Vibration damping
- Heat insulation
- Oil and chemical resistance
- Mechanical resistance (including abrasion resistance)
- Functionality in low and elevated temperatures
- Weather and ozone resistance
- Impermeability for gases and fluids
- Elasticity and vibration damping properties
• Long-term creep
• Processability

**Dimensioning of elastomer products**

In dimensioning the most important starting points to be taken into account in early stage of design are

• Functionality
• Prediction and ensuring the risks of damage
• Prediction of lifetime

To predict the damages, it is important to know models of behaviour and parameters of materials. Models of planning are not very advanced for elastomers. Exploitation of those is complicated because of non-linear loading-deformation phenomena that make the theoretical prediction of practical structures difficult.

**Product shaping**

As a result of dimensioning, certain limitations for products' dimensions have been achieved. Before the mould design the structure of the elastomer product has to be shaped so that the local stresses are avoided in loading situations. The weather sensitive surfaces should not be exposed to stretch loadings.

**Recycling and reuse of elastomeric materials**

The global consumption of vulcanized elastomers is about 17.2 million tons/year. Approximately 40% of that is natural rubber.

The main problem with vulcanized rubber products is their use after their useful life has expired. Rubber waste is usually generated from both the products of the manufacturing process and post-consumer products, mainly consisting of scrap tires.

The environmental problems created by waste rubbers and legislative restriction demands search for economical and ecological methods of recycling.
### Recovery Alternatives

<table>
<thead>
<tr>
<th>Kind of recovery</th>
<th>Recovery process</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Product reuse</strong></td>
<td></td>
</tr>
<tr>
<td>Repair</td>
<td>Retreading</td>
</tr>
<tr>
<td></td>
<td>Regrooving</td>
</tr>
<tr>
<td>Physical reuse</td>
<td>Use as weight</td>
</tr>
<tr>
<td></td>
<td>Use of form</td>
</tr>
<tr>
<td></td>
<td>Use of properties</td>
</tr>
<tr>
<td></td>
<td>Use of volume</td>
</tr>
<tr>
<td><strong>Material reuse</strong></td>
<td></td>
</tr>
<tr>
<td>Physical</td>
<td>Tearing apart</td>
</tr>
<tr>
<td></td>
<td>Cutting</td>
</tr>
<tr>
<td></td>
<td>Processing to crumb</td>
</tr>
<tr>
<td>Chemical</td>
<td>Reclamation</td>
</tr>
<tr>
<td>Thermal</td>
<td>Pyrolysis</td>
</tr>
<tr>
<td></td>
<td>Combustion</td>
</tr>
<tr>
<td><strong>Energy reuse</strong></td>
<td>Incineration</td>
</tr>
</tbody>
</table>
SUMMARY

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1. Polymers

1.1. Natural rubber (NR) is obtained from latex, and the basic steps to get the polymer are tapping of the latex, dilution, coagulation of the polymer and drying. It is basically polymerized isoprene. As a natural product it’s properties are influenced by environmental and seasonal variations, and it always contains a certain percentage of impurities. Natural rubber has one unique property: it shows strain crystallization; this makes the material exceptional strong. Other characteristic properties are good rebound properties, low damping, low hysteresis, low heat built-up at dynamic deformations, very good set-properties, all due to a high network density, but poor ageing and ozone resistance caused by the unsaturation in the backbone. NR also has poor oil resistance.

1.2. Isoprene rubber (IR) is the synthetic counterpart of NR, but the properties of IR are significantly different from the properties of NR: IR is easier processable in terms of mastication and mixing, it has a lower die-swell and storage hardening. Only in compression set behavior is IR better than NR, in most other properties is IR inferior. One reason for the differences in properties is the composition of the material: IR is a relatively pure material, and it never contains 100% of the cis-1,4 polymer as NR does.

1.2. Butadiene rubber (BR) is characterized by a very narrow molecular weight distribution in comparison to NR and other synthetic rubbers. Therefore it shows a high degree of coldflow (flow of the bale during storage). The most important properties of BR are:

- Lowest Tg of all rubber polymers (-100°C – (-90°C));
- Very high network densities after sulfur vulcanization, due to the high degree of unsaturation. This results in a high abrasion resistance, good elasticity, good tear strength at dynamic deformation, good elasticity at low temperatures, low heat build up (important for tire applications).
- Low wet-traction or friction coefficient for tires on a wet road, low tensile strength (no strain crystallization).
1.3. Styrene-Butadiene rubber (SBR) is by far the most important synthetic rubber. The butadiene content makes it sulfur-vulcanizable and gives rubber-elastic properties; the styrene accounts for the damping, needed for the skid resistance of tires. Butadiene and styrene are randomly distributed throughout the molecular chain. The styrene content lies between 23 – 40%, depending on the SBR type. Another important parameter is the way in which the butadiene monomer is built in: cis, trans or vinyl. The cis-type is the most flexible (see also NR and BR) one, the trans type is a bit less flexible and the vinyl configuration is the least flexible.

Emulsion-SBR (E-SBR), polymerized in the cold process, has app. 9% cis- and 76% trans-configuration; the remaining 15% are 1,2-vinyl addition products. With increasing styrene content the following properties change:

- The polymerization time decreases;
- Gel formation decreases (gel formation occurs via the butadiene moiety);
- The T_g rises;
- The wet skid-resistance of tires is improving (poorer network because of less butadiene);
- The ozone resistance is improving (less unsaturation);
- Tensile strength and abrasion resistance deteriorate (poorer network);
- The rolling resistance of the tires gets worse (poorer network).

The most important aspects of E-SBR are:

- No strain-crystallization like NR; in order to obtain good mechanical properties, reinforcement with highly reinforcing blacks or silica’s is needed. Black-filled SBR compounds nevertheless show lower tensile strength, clearly lower tear strength and elasticity than NR;
- Skid resistance of tire treads is clearly better than with NR, because of the worse network;
- High heat built-up upon dynamic deformation (poorer network);
- Better fatigue and heat resistance than NR (less unsaturation in the main chain).

Solution-SBR (S-SBR) shows significant differences to E-SBR: the solution polymerization of SBR provides for a narrower molecular weight distribution and additionally a remarkably higher cis-1,4 content of the butadiene. This gives better elastic properties of the networks of S-SBR, among others less dangling ends. Furthermore, the solution polymerization technique offers the manufacturer more possibilities to govern the desired polymer structure.
1.4. Ethylene-propylene-diene rubber (EPDM) and its saturated counterpart EPM are almost random polymers. Contrary to the homopolymers of ethylene and propylene, EPM behaves amorphous and rubbery.

The ratio ethylene / propylene in commercial products lies between 75/25 and 45/55 by weight. The high ethylene EPM’s are crystalline types; low ethylene EPM’s are called amorphous types.

EPM can only be vulcanized with peroxides as it is fully saturated. EPDM has an unsaturation in the side chain from the diene component (mostly 5-Ethylidene-2-norbornene, ENB) giving it a very good aging resistance.

The most important properties of EPDM are:
- Exceptional ozone and ageing resistance because of the saturated backbone;
- Can be highly filled with filler and oil, due to the high green strength obtained from the crystallization of high ethylene sequences (results in cheap mixtures);
- EPDM can be vulcanized with sulfur, but in comparison with NR or BR is it quite difficult. It requires a vulcanization temperature that is about 15 degrees higher, a lot of (ultra-) accelerators and still a small amount of crosslinks are formed. The final network density which can be achieved is limited;

1.5. Butyl rubber (isobutylene-isoprene rubber, IIR) is a specialty rubber that is used in inner tubes because of its low gas permeability. IIR is built out of poly-isobutylene and 1-5 %wt isoprene. The polymer structure (dimethyl substitution on every second carbon atom of the chain and low level of unsaturation) determine the main properties of butyl rubber:

- Low gas permeability;
- Reasonable resistance to ozone, oxygen and heat ageing;
- Good resistance to chemicals;
- Low elasticity.

Nowadays, an ever-increasing amount (more than 50 %) of halogenated (chlorinated, CIIR, and brominated, BIIR) butyl rubber is used in industry, because it has more affinity with high-unsaturation rubbers.

1.6. Butadiene-acrylonitrile rubber (NBR) distinguishes itselfs from NR and SBR in its good resistance against non-polar substances like gasoline, diesel fuel, oils and fats, good ageing resistance and good resistance to chemicals. The physical and technological characteristics of NBR are closely related to the ACN-content. With increasing ACN-content,
- Vulcanizates have better resistance against swelling in gasoline, diesel fuel, oils, fats and organic solvents;
- The polymer is better miscible with polar plasticizer and polar solvents;
- The polymer is better miscible with polar synthetic materials, like PVC;
- The polymer is better miscible with compounding ingredients;
- The elasticity and cold-flexibility get worse.

**HNBR** is produced by selectively hydrogenating the butadiene double bonds of NBR. It combines the oil resistance of NBR and the oxidation, ozone and ageing resistance of EPDM.

### 1.7. Chloroprene rubber (CR)

has a high percentage of trans-1,4 addition products that gives the material the ability to strain-crystallize. It shows

- Medium oil resistance;
- Medium resistance against chemicals;
- Limited resistance against weathering, ageing and ozone;
- Good flame-resistance properties, because of the chlorine atom.

Contrary to the other diene rubbers, CR is vulcanized with metal oxides like MgO and ZnO, not with sulfur.

### 1.8. Fluororubbers (FKM)

are co- and terpolymers consisting of at least 75% vinylidene fluoride with hexafluoropropene, tetrafluoroethylene, 1,2,3,3,3-pentafluoropropene or trifluoromethyl-trifluorovinylether as comonomer. Vulcanization is done with diamines in combination with basic metal oxides (MgO). Fluororubbers allow the highest use temperatures, up to 240°C. These products have a very good oil resistance. The mechanical properties, the elasticity and the cold flexibility of FKM are their weaker points, besides the high prize.

### 1.9. Silicone rubber (Q)

properties are strongly dependent on the substituents:

- R1, R2 = methyl: bad cold flexibility;
- R1, R2 = phenyl: improved cold flexibility;
- R1 = methyl, R2 = vinyl: good compression set;
- R1 = phenyl, R2 = vinyl: good compression set;
- R1 = vinyl, R2 = trifluoropropyl: good oil resistance.

In general the silicone rubbers distinguish themselves by a good high temperature, ozone and UV resistance, good cold flexibility, little temperature dependence of the mechanical properties, low Mooney viscosities at high molecular weights and high gas permeability. The Si-O bond can be hydrolyzed by strong acids and bases. In order to improve the strength of the vulcanizates, highly reinforcing filler is added, mostly pyrogenic silica.
There are two types of silicone rubbers, depending on the vulcanization temperature: warm vulcanizing (HV-types) and room temperature vulcanizing (RTV).

2. Fillers

2.1. Fillers in general

There is a distinction between active or reinforcing fillers, and non-active or non-reinforcing fillers. With activity or reinforcement, commonly all kinds of rubber/filler interactions are described which express themselves in physical properties that can be measured. More specific, the term reinforcement is used for an increase in tensile strength and/or improvement of abrasive properties. The emphasis in rubber compounding is on reinforcing fillers, especially carbon black and silica.

A precondition for filler reinforcement is the interaction between the filler particles and the polymer. These interactions can be strong, for example in the case of covalent bonds between functional groups on the filler surface and the polymer, or weak as in the case of physical attractive forces. When carbon black is blended with a polymer, the level of physical interaction is high. In contrast to this, the interaction between silica particles and the polymer is very weak, and only by the use of a coupling agent a bond is formed between the filler and the polymer.

Besides the interaction between polymer and filler, an interaction between filler particles occurs, predominantly above a critical concentration threshold, the percolation threshold: The properties of the material change drastically, because a filler-filler network is established. This results for example in an overproportional increase of electrical conductivity of a carbon black filled compound. But even at lower concentrations, the filler-filler interactions influence the material characteristics.
 Mixing of rubber is not just a process with the aim of a homogenous distribution of the compound additives in the polymer matrix, but includes processes such as plasticization, incorporation of solids and dispersion. During mixing all these processes take place, but depending on the mixing parameters and the degree of mixing the rate of the different processes changes. On macroscopic scale the dispersion of a filler into a polymer matrix shows the following stages (see also Figure 2-1):

- The filler smears into striations following the deformation pattern of the polymer;  
- Agglomerates up to 10 to 100 micrometer in size appear;  
- Agglomerates are continuously broken and aggregates with an average size of 100 nanometers till 0.5 micrometers appear  
- Smaller aggregates and primary particles appear on the expense of larger aggregates and agglomerates.

The filler forms a network in the elastomer matrix. On deformation, this filler network is easily disturbed, while the rubber network remains intact. An example of this is the so-called Payne-effect: the elasticity modulus of reinforced rubber depends on the magnitude of the deformation. On increasing strains, the E-modulus decreases. Especially at dynamic mechanical deformations (cyclic sinusoidal deformations), it is clear to see that $E'$ and $E''$ depend on the amplitude of the deformation. One explanation of the Payne-effect deals with the destruction-reformation of the percolating filler network upon deformation of the rubber. This can as well involve polymer bound to the filler surface.

**Bound rubber** is defined as polymer attached to the surface of the filler particles. If unvulcanized black-filled rubber is extracted with a good solvent, part of the rubber appears to be insoluble. This fraction remains as a hard, brittle gel bound to the carbon black and it is filtered off along with the carbon black. This fraction is called the bound rubber. It is caused by the interaction between the black particle and the rubber as a result.
of adsorption, various sorts of chemisorption, bonding between free rubber radicals, etcetera.

2.2. Carbon black
An important quantity that determines the reinforcing effect of a filler is the amount of surface area per gram filler. This quantity is mainly determined by the dimensions of the primary particles. These dimensions determine how much contact area is available for interaction between the filler and rubber. The specific surface area of fillers is normally determined by standard techniques, in which the adsorption of gas (N₂: BET-method), Iodium or cetyl-trimethylammonium bromide (CTAB-method) is measured. As an example, typical values for the specific surface area of different types of carbon black are appr. 6-160 m²/g black.

During mixing, a reinforcing filler is mainly broken down to the dimensions of aggregates, the aggregate structure being another important factor. The structure differs from ‘strings of pearls’ to ‘grape bundles’ of primary particles. The empty volume within these structures is measured by filling it with a liquid, i.e. dibutylphtalate: The higher the structure of a filler, the higher is the DBP absorption. There is a relation between the DBP absorption and the reinforcing effect of the filler: With equal crosslink density, the 300% Modulus increases on increasing DBP-number if blacks with the same specific area are used.

The specific surface activity is another important factor. The type of linkage that is formed at the surface of the filler with the rubber, has been the subject of many studies, but has not been fully elucidated. Some researchers reason about chemical bonds between e.g. the carbon black and the rubber molecules, others reason about physical absorption. The absorptive active surface comprises only 5% of the total available surface. Even without covalent chemical bonds, reinforcement is observed; though, the presence of chemical bonds works in a positive way.

The great variety of blacks requires a classification, in order to realize a possible interchangeability between the different suppliers. In 1967, a consequent classification has been introduced by the ASTM (American Standards Association). A nomenclature was set up, consisting of a letter and three digits: N and S respectively, for Normal and Slow curing (Channel and post-oxidized black). The first of the three digits corresponds with the diameter of the primary particle size, ranging from 1 to 9. The following two digits were chosen randomly and do not have a specific meaning.

2.3. Silica
Silicas, which are used in rubber reinforcement, have a specific surface area of 25 – 250 m²/g, comparable to the surface area of carbon blacks. In the rubber industry, mainly the cheaper precipitated silicas are used.
The surface of silica is covered by a layer of acidic silanol groups and different siloxane groups: geminal, vicinal, clustered and isolated groups. The functional groups are randomly distributed over the whole surface, in contrast to carbon black, where the functional groups are preferably located on the edges of the crystallites. The silanol groups on the surface of different silica particles interact with each other, resulting in strong agglomerates due to the hydrogen bonds between the silanol groups. The moieties on the silica surface also interact with basic accelerators, resulting in reduced curing rates and lower crosslink densities. They can react with other chemical compounds such as stearic acid, polyalcohols and amines. These compounds compete with the coupling agent for adsorption sites on the filler surface; reduce the concentration of free surface silanol groups and thus the silanization efficiency.

Silica compared to carbon black is characterized by weaker filler-polymer interactions and stronger filler-filler interactions. This results in a higher compound viscosity, a higher modulus at low strain amplitudes, a lower modulus at high strain amplitudes and a lower bound rubber content. However, the combination of silica with a coupling agent has a higher reinforcing effect and different dynamic mechanical properties compared to carbon black. The main influence on the mechanical properties when replacing carbon black by silica combined with a coupling agent is found for:

- Tear, abrasion and heat resistance
- Flex stability
- Hardness, stiffness and modulus-Tack
- Heat build up
- Resilience

The stronger reinforcing effect of silica compared to carbon black allows the reduction of the filler content without any negative influence on the property profile, but with an additional positive effect on elasticity due to the higher ratio of elastic component to damping filler. This results in an additional reduction of the rolling resistance.

The formation of a hydrophobic shell around the silica particle by the silica-silane reaction during mixing prevents the formation of a filler-filler network due to the reduction of the specific surface energy. The chemical reaction of silica with an alkoxy-silyl moiety of the coupling agent takes place in a two-step, endothermic reaction. The primary step is the reaction of alkoxy-groups with silanol groups on the filler surface. The secondary reaction is a condensation reaction between adjacent molecules of the coupling agent on the filler surface or between alkoxy-groups of the coupling agent and silanol groups of the silica. It is generally accepted, that a hydrolysis step is involved in the reaction. In comparison to the primary reaction this step is slower with a factor of approximately 10.
The coupling agents need a moiety enabling them to react with the polymer during vulcanization in order to be reinforcing. In general, the moiety reacting with the polymer is a sulfur-group, either a poly- or disulfidic group or a blocked sulfur-group. Other functional groups used to link the coupling agents to the polymer are double bonds, which have to be activated by the addition of an active sulfur-compound or by the generation of a radical moiety in order to have a simultaneous crosslinking of the polymer and the coupling agent with comparable reaction rates during curing.

In the rubber industry, silica has its main application for 65% in shoe soles, 25% in tires (but this area shows a strong increase over the latest years) and about 10% in technical goods. Nowadays there is a strong increase in the use of silica in tires, because silica in combination with S-SBR offers the possibility to reduce the rolling resistance with 30%. This is achieved because of a lower hysteresis, while the wet skid resistance, wet traction and snow behavior remain at the same level. This results in fuel savings of about 5%.

2.4. Mineral fillers

Besides the reinforcing fillers, there is a wide range of non-reinforcing fillers, which all have a common main property: making black and non-black compounds cheaper.

- Whiting: milled, washed and precipitated. They differ somewhat in color and in their effect on the processability and vulcanization. It is possible to prepare calcium carbonate with very small particle diameter, which has a semi-reinforcing effect. Some of the whiting types have been treated with ca. 3 % stearate to increase miscibility and dispersibility;
- Kaolin, or clay. Soft clays or hard clays, calcined clays and treated clays. Some are pure fillers without further reinforcement; others have BET-surfaces of 20-50 m²/g and show a bit reinforcement;
- Aluminum-trihydrate: less used as filler as such, but more because of its capability of splitting off water at elevated temperatures and in this way to act as a flame retardant. However, such high loadings are needed in the recipe that many of the elastic properties are lost;
- Talc and micro-talc. A finely milled mineral, mainly built up of Mg- and Al-silicate. It is very inert filler and it is mainly used in heat-resistant compounds for sleeves, autoclave-sealings, etcetera. Talc is so inert, that it is used in large quantities as release agent. It prevents sticking of rubber surfaces onto each other, or other surfaces;
- TiO₂: white coloring agent, somewhat reinforcing;
- Many others.
3. Plasticizers and extender oils

Plasticizers are normally added to the compound to increase the processability of the compound. As a result of the addition of the reinforcing fillers, the viscosity increases so much that the compound cannot be processed anymore. If, on the other hand, less filler is added to the compound, less reinforcement is obtained, or we have a very expensive compound. In most cases, the prizes of fillers are lower than those of the pure elastomers. The compounders will therefore always try to add a maximum of filler, and subsequently account for the processability-loss by adding the desired amounts of plasticizers and extender oils.

Mineral oils, or oils directly obtained from crude oil refining, are by far the most widely used plasticizers. Depending on the character of the crude oil, various types of oil can be obtained. In the oil industry, the oils usually are classified according to their density (or specific gravity) and their viscosity. In this way, an unambiguous specification can be obtained: the so-called Viscosity Gravity Constant, or VGC. The various types of oil can be distinguished very well with this characteristic, see Table 3-1.

**Table 3-1: Relation between VGC and the content of mineral oils.**

<table>
<thead>
<tr>
<th>Type of oil</th>
<th>Range of VGC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffinic</td>
<td>0.791 – 0.820</td>
</tr>
<tr>
<td>Relatively naphtenic</td>
<td>0.821 – 0.850</td>
</tr>
<tr>
<td>Naphtenic</td>
<td>0.851 – 0.900</td>
</tr>
<tr>
<td>Relatively aromatic</td>
<td>0.901 – 0.950</td>
</tr>
<tr>
<td>Aromatic</td>
<td>0.951 – 1.000</td>
</tr>
<tr>
<td>Strongly aromatic</td>
<td>1.001 – 1.050</td>
</tr>
<tr>
<td>Extremely aromatic</td>
<td>&gt; 1.050</td>
</tr>
</tbody>
</table>

In general, one can state that the polar plasticizers/oils are compatible with polar rubbers and that non-polar plasticizers/oils are compatible with apolar rubbers, see Table 3-2. The amount of plasticizers in rubber varies from 5 –30 phr for natural rubber or SBR-compounds, till more than 100 phr for EPDM.
For the more polar rubbers NBR and CR it is difficult to find a compatible mineral oil. Therefore, one also applies **synthetic plasticizers** in these compounds, despite their high cost prize. Because of the great variety in composition and specific chemical functional groups, there is a large number of these plasticizers on the market. Most of them are meant to obtain specific properties in the vulcanizates:

- Phthalic acid esters, mainly dibutyl- (DBP), dioctyl- (DOP), diisooctyl- (DIOP) and diisononyl-phtalate (DINP). Phthalic esters are especially suitable for NBR and CR compounds, to improve their elasticity and low-temperature flexibility. At higher molecular weights, low temperature properties are adversely affected. Amounts: 5 – 30 phr.

- Adipinic acid esters, for instance dioctyl adipate. These are more expensive than phthalic acid esters, but give better low temperature flexibility, especially for NBR.

- Phosphoric acid esters: chemicals like tricresyl- and diphenylcresyl-phosphate, sometimes mixed with trixylyl- or trioctyl-phosphate. The phosphoric acids are especially used because of their low flammability, especially in rubber which already has a low flammability, like CR.

- Chlorinated carbohydrates: chlorinated paraffines are added in amounts of 20 phr to decrease the flammability of rubber vulcanizates. When bigger amounts are used, the properties of the vulcanizates decrease too much. In CR usually only 10 phr is added.

- Polycondensated products: polyesters from adipinic or sebacinic acid and 1,2-propyleneglycol are used because of their high molecular weights and their still liquid behavior as a non-volatile, non-migrating plasticizer. They are specially used in NBR.

### Table 3-2: Compatibility of mineral oils with the different types of rubber.

<table>
<thead>
<tr>
<th></th>
<th>NR</th>
<th>SBR</th>
<th>BR</th>
<th>NBR</th>
<th>CR</th>
<th>CSM</th>
<th>EPDM</th>
<th>IIR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffinic</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Relatively naphtenic</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Naphtenic</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>+</td>
<td>0</td>
</tr>
<tr>
<td>Relatively aromatic</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>0</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Aromatic</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>Strongly aromatic</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>0</td>
<td>-</td>
</tr>
</tbody>
</table>
4. Vulcanization

4.1. Sulfur-vulcanization

When a mixture of natural rubber and free sulfur is heated up, most probably free radicals are formed as a result of the ring opening of the eight-membered sulfur rings, which can react afterwards with the unsaturation of the natural rubber. An extremely diverse mixture of inter- and intramolecular sulfur-bridges is formed. Some of these sulfur-bridges develop to real network crosslinks, while some of them are spoilt, because they become linked to the same polymer chain at both ends (see Figure 4-1).

In sulfur curing, activators are used together with accelerators: it speeds-up the reaction remarkably. However, it works in particular if the ZnO is made soluble by adding small amounts of acids, especially fatty acids like stearic acid. Besides this, sulfur accelerators are used to further enhance the vulcanization reaction and to tailor the sulfur network structure. In cases, that scorch leaves no time for enough processing and that preliminary scorch is observed, vulcanization retarders may be added to the compound. Volatile organic acids or derivatives are often used for this purpose (benzoic acid, phthalic anhydride, and salicylic acid).

With the vulcanization of very thick articles, like tunnel sealings, fenders, large tires etc. the outer shell of the article very often is over-cured while the inner part is under-cured. One way to reduce this effect is to vulcanize at very low temperatures for very long times, or to use anti-reversion chemicals.

Accelerators (see Table 4-1) react in a different way with various elastomers. For instance, NR-compounds react different from EPDM compounds due to the difference in unsaturation between the two polymers: EPDM requires a higher accelerator concentration and, in order to avoid blooming, a higher number of different accelerator types.

**Figure 4-1: Model of an ‘accelerated’ NR-sulfur network.**

\[ S_1 = \text{monosulphide} \]

\[ S_2 = \text{disulphide} \]

\[ S_n = \text{polysulphide} \]

\[ S_m = \text{main chain bound sulphur chains} \]

\[ S_{H} = \text{thiol groups} \]

\[ S_{ac} = \text{sulphur donor accelerator residues} \]

\[ C = \text{carbon-carbon crosslinks} \]

\[ Sm = \text{cyclic sulphur structures} \]
Table 4-1: Accelerator types

<table>
<thead>
<tr>
<th>THIAZOLEMBT</th>
<th>SULFENAMIDES CBS</th>
<th>GUANIDINES DPG</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Thiazoles (MBT)" /></td>
<td><img src="image" alt="Sulfenamides (CBS)" /></td>
<td><img src="image" alt="Guanidines (DPG)" /></td>
</tr>
</tbody>
</table>

4.2. Peroxide-vulcanization

Since the beginning of last century it is known that polymers can be vulcanized by means of peroxides. The possibilities to achieve crosslinking with peroxides are very divers. Almost all polymers, that do not tend to decompose under the influence of radicals, can be crosslinked with peroxides. Unsaturated bonds are not necessary for peroxide vulcanization. It is therefore a vulcanization technique that has gained importance since the introduction of fully saturated polymers like EVA (ethylene-vinylacetate), EPM, EPDM, CM (chlorinated polyethylene) and Q. For NR, SBR and NBR, peroxide vulcanization is only applied on small scale. This is due to the fact that these unsaturated polymers need to be stabilized by means of antiozonants and antioxidants. In general, these antidegradants are very strong radical scavengers. It will be clear that the application of these antidegradants conflicts with peroxide vulcanization, that proceeds according to a radical mechanism.

Usually, peroxides are divided in two categories:
- Peroxides with carboxy-groups, with diacetylperoxide as aliphatic example and dibenzoylperoxide as aromatic example;
- Peroxides without carboxy-groups, with di-tert.butylperoxide as aliphatic example and dicumylperoxide as aromatic example.

Besides symmetric peroxides, there are also combinations of different sorts of peroxides, asymmetric peroxides. An example of an asymmetric peroxide is t-butyl cumylperoxide. Symmetric peroxides have in general a higher efficiency than the asymmetric types.

The yield of crosslinks in peroxide-curing can be increased coagents. These are polyvalent substances that bring about several consecutive reactions at the peroxide
decomposition. Examples of these coagents are di- or triallylic substances, maleimids or reactive acrylic-substances.

Peroxide-vulcanizates are tougher than sulfur-vulcanizates, leading to lower tensile properties, lower elasticity and worse dynamic properties. On the other hand, the heat resistance of peroxide-vulcanizates is remarkably better compared to sulfur-vulcanizates. This is due to the high dissociation energy of the C-C bond. Also the compression set is in general better for peroxide-vulcanizates than for sulfur-vulcanizates.

4.3. Other vulcanization systems
- ZnO and/or MgO for CR: for CIIR and BIIR;
- Polymethylol-phenol resin: for IIR;
- Amines and polyamines: for FKM and ACM.

5. Anti-oxidants, anti-ozonants

Rubber compounds can be degraded by reactions with oxygen, ozone, light, metal ions and heat. Antidegradants protect rubber against aerobic aging (oxygen) and ozone attack. They are of prime importance and play a vital role in rubber products to maintain the properties at service conditions.

Degradation by oxygen and ozone proceeds via different chemical mechanisms and results in different effects on physical properties of rubber:

- Ozone degradation: discoloration, cracking (primarily a surface phenomenon)
- Oxygen degradation: hardening or softening (depending on the base polymer) throughout the rubber article

Five general modes of oxidation inhibition are commonly recognized: Metal deactivators, light absorbers, peroxide decomposers, free radical chain stoppers and inhibitor regenerators.

Ozone resistance is improved by use of chemical antiozonants and via several physical methods which protect under static conditions. This can be accomplished by adding paraffinic and microcrystalline waxes to the rubber and/or adding an ozone resistant polymer that increases the critical stress (EPM, EPDM, halobutyl, polyethylene, polyvinyl acetate).
Chemical antiozonants have been developed to protect rubber against ozone under dynamic conditions. The most effective antiozonants are substituted paraphenylenediamines, PPD’s.

Table 5-1 gives some examples of antidegradants.

<table>
<thead>
<tr>
<th>Table 5-1: Some examples of antidegradants</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Paraphenylenediamines</strong></td>
</tr>
<tr>
<td>General formula</td>
</tr>
<tr>
<td><img src="image1" alt="Formula" /></td>
</tr>
<tr>
<td>Most effective antidegradants for all general purpose rubbers</td>
</tr>
</tbody>
</table>

| **Diphenylamines**                        |
| General formula                           |
| ![Formula](image2)                        |
| For all general purpose rubbers. Good heat protection, esp. in CR |

| **Naphtylamines**                         |
| Phenyl-a-naphthylamine (PAN)              |
| ![Formula](image3)                        |
| Highly effective antioxidants, but toxicological risk |

| **Dihydroquinolines**                     |
| 2,2,4-Trimethyl-1,2-dihydroquinoline, polymerized (TMQ) |
| ![Formula](image4)                        |
| n (n=ca. 3)                               |
Processing of Elastomeric Materials
Virtual Education in Rubber Technology (VERT), FI-04-B-F-PP-160531

SUMMARY

Läroverket AB
info@laroverket.com

1. Rubber

In this chapter polymers are divided into General Purpose Polymers and Special Polymers, divided into two categories, used in high volumes and low volumes. A brief description of the polymers, datasheets and a summary of properties are given.

Natural Rubber (NR), Isoprene Rubber (IR), Styrene Butadiene Rubber (SBR) and Butadiene Rubber belong to the General Purpose Polymers. Ethylene Propylene Rubber (EPM and EPDM), Butyl Rubber (IIR), Acrylic Nitrile Rubber (NBR) and Chloroprene Rubber (CR) belong to Special Polymers used in high volumes.

All rubber elastomers have to be cured to obtain the expected mechanical and chemical properties. The chemistry for curing, the process when rubber mixed with curing agents under the influence of heat and pressure change from plastic to elastic state, is described.

2. Thermoplastic elastomers

A blend of rubber and thermoplastic polymers is called Thermoplastic elastomers. Its physical properties are very alike those for cured rubber though thermoplastic elastomers do not need curing to obtain those properties.

The classification of thermoplastic elastomers is given as well as the differences in structure between cured rubber and thermoplastic elastomers. Thermoplastic elastomers can be recycled which is not the case with rubber.

Thermoplastic elastomers is a group of material being a blend of rubber and thermoplastic polymers, which have physical properties very much cured rubber, but do not need curing to obtain the properties. The classification of that group of material is given and the different structure between cured rubber and thermoplastic elastomers is presented. In opposite to cured rubber, thermoplastic elastomers can be recycled.
3. Processing methods for rubber

3.1 Mixing

The first step when processing rubber is to make a compound, mainly consisting of one or two or three polymers, reinforcing agent (e.g. carbon black), softener, curing agents and antioxidants.

There are three different kinds of mixing machineries; mixing mill, internal mixer and continuous mixer of which the internal mixer is the most common. The first step in processing of rubber is to make a compound mainly consisting of rubber polymer, reinforcing agent as carbon black, softener, curing agents and antioxidants. Three different types of mixing machinery are available: mixing mills, internal mixers and continues mixers of which the internal mixer is the most common.

This type of machinery consists of two rotors in an enclosed chamber. The rotors are shaped so that they have a kneading effect while at the same time the chamber ensures that all the materials which are added remain in place.

An internal mixer line consist of systems for weighing raw materials and transport them into the mixer, the internal mixer, extruder or mills to make sheets of the compound after it is dumped from the mixer and a cooling line.

The mixing of rubber is a complicated process that involves a number of different mechanisms and stages. The steps may be separated into four basic processes.

The mixing of rubber is a composite operation, involving a number of different mechanisms and stages. The steps can be divided into four basic processes:

- Viscosity reduction
- Incorporation
- Distributive mixing
- Dispersive mixing

The mixing process is done at an elevated temperature as the operation itself generates a high temperature.

When the compound is cooled down to room temperature and is tested it will be ready for the next manufacturing step.
3.2 Textile treatment

Many rubber products consist of a combination of rubber and reinforcing materials, e.g., textile or steel wire. To mention the most well-known products, tyres, hoses and belts. For these products it is essential that the reinforcing material is stable at curing temperatures and to achieve a good bonding between rubber and the reinforcement during the curing process.

For textile reinforcing materials, woven fabrics or cord fabrics, the ordinary process includes dipping the textile in an adhesive solution of rubber latex, resorcinol and formaldehyde. The solution is cured and the textile stabilizes when heating it to high temperature under tension, so called Hot Stretching. The reinforcing fabric is then ready to be covered with rubber compound.

Many rubber products are a combination of rubber and force up taking reinforcing materials as textile or steel wire. Typical well-known product areas are tyre, hose and belts. In all this products it is essential to make the reinforcing material stable at curing temperatures and to treat the materials for a good bonding between rubber and reinforcement during the curing process.

For textile reinforcing materials, in the form of a woven fabric or a cord fabric, the normal process includes dipping the textile in an adhesive solution of rubber latex, resorcinol and formaldehyde after which the solution is cured and the textile being stabilized by heating it up to a high temperature under tension, a process commonly called Hot Stretching. After that treatment the reinforcing fabric is ready to be covered with a rubber compound.

3.3 Calandering

Calendering is a process where rubber compound is formed into a continuous sheet or coated on a fabric. The figure below shows configurations of the rolls in a calendar and also gives examples of the use of each machine. The number inside the rolls indicates the ratio of the speed of each roll.

Calendering is a process where rubber compound is formed to a continuous sheet or coated on a fabric. This is done by feeding the rubber compound to one or several on each other following roll gaps. The figure shows different configurations of the rolls in a calender and also gives examples of the use of respective machine. The numbers inside the rolls describes the ratio of the speed of each roll.
The rolls is mounted in a heavy frame with separate driving units for each roll, and the machinery is placed in a manufacturing line with feeding equipment for rubber and fabrics as well as cooling rolls and rolling up devices.

Calendering is used in the manufacturing of a multitude of products either for rubber coatings of fabrics or for the preparation of sheet products. Rubber coating is an important process of manufacturing i.e. tyres, conveyor belts, hoses and footwear. Sheet preparation is used for the same products as mentioned and for all kind of technical rubber sheeting. Perfect sheets up to 2 mm thickness can be produced without air inclusions. For thicker sheets a combination of an extruder and a calendar is used, so called Roller Head Calender.

3.4 Spreading

Beside calandering, fabrics can also be coated with rubber by a spreading technique. In the spreading process, the rubber compound is dissolved in a suitable solvent to achieve the consistency of dough.

When calendering the total thickness of the coating is normally obtained in one passage in the machine. While spreading, the total thickness is normally built up by several passages and evaporation of the solvent between each passage.

The dough used has normally a dry content of about 50 - 60 % and the rest is solvents. The solvents used by manufacturing the dough are determined by the rubber type to be solved and the evaporation speed wanted. Another important criterion is the health risk with the solvent.

The spreading machine has a design shown in the principle figure below. It consist mainly of, an let-off roll, a spreading part with a doctor knife, a drying zone with steam heated plates and an take up roll. The evaporated solvents are taken to a recovery unit or adsorbed in a filter.
3. 5 Extrusion

Extrusion is one of the rubber industry most common methods of processing. Products or half fabricates produced by this method have a cross section that is determined by the shape of a die but can vary in length. The machine used to form the product is called an extruder, which could be considered as a powerful pump in which a screw is pumping the rubber material towards the die in which the shape of the extrudate is determined.

Extruders are used for shaping ready products or parts to be used in a later operation like inner tube for hoses, blanks for feeding of moulds, parts for tyre building and tyre inner tubes.

In most cases the extruder is fit with a long screw having a length of 16 to 24 times of the diameter. The long screw makes it possible to feed the extruder with cold rubber as it will be heated up to suitable temperature by the shear forces generated in the screw.

3. 6 Mould curing

Moulding is preferable for volume production of products with closed dimensional tolerances. Sealing rings and bellows etc are typical examples of such products. Tyres may however be considered as a moulding product too. Moulding and curing are carried out in the same process. The moulding is done when the rubber fills the cavities of the mould, while the curing is done subsequently by heating the rubber in the mould.
Three basic techniques are used for mould curing, the selection of technique mainly depending on product size, material to be used, dimensional accuracy and the length of production. The methods are called Compression moulding, Transfer moulding and Injection moulding.

The moulds used to shape the product are made of steel and mounted in hydraulic or mechanical presses able to close the moulds with a high pressure. The moulds are heated up by steam, electrically or by hot water to a temperature of normally 160 – 200 °C.

The three different methods are described in the following principal sketches.

Nearly all moulded products have flash along the mould parting lines which has to be removed in a separate operation.

In many cases it is economical and in other cases technical needed to post-cure the moulded product in a heated oven.

As the thermal linear expansion for rubber is much higher than for steel a mould cured rubber product will shrink approximately 2 % when cooled which has to be taken into account when manufacturing the mould.
3. 7 Rubber metal bonding

In many cases, it is desirable to be able to apply rubber to metal, e.g. when rubber is used for corrosion or wear protecting linings or for the covering of rolls. In many engineering parts such as dampers, couplings, solid rubber wheels or sealing rings, rubber is combined with metal.

One of the most vital properties for that type of rubber is the bonding between rubber and metal.

The common way to achieve a good bonding is to do an extra ordinary good cleaning. The metal is then blasted and prepared with a bonding agent dissolved in a solvent or in water.

Rubber to metal bonding agents, both the primer and the adhesive, usually contain a mixture of resins, polymers, curatives, extenders, pigments, corrosion inhibitors and viscosity stabilisers.

The primer contain organic resins, halogenated polymers, fillers like titanium dioxide, zinc oxide and aluminium silicates which reacts with most metallic materials (carbon steel, stainless steel, aluminium, brass etc) to form chemical bonds with the metal during the vulcanisation.

The curing of the rubber metal products can be carried out in all common curing techniques preferable under pressure.
3. 8 Vulcanization

Beside of mould curing, rubber products can be cured by several methods. The most important methods are:

Beside mould curing rubber products can be cured by several methods of which the most important are:
Autoclave curing in steam or air.
Continuous curing of extruded products and cables.
Continuous curing of calendered products.

Autoclave curing is used for a large variety of purposes e.g. vulcanisation of extrudates, vulcanisation of large products unsuitable for moulding, forming of extrudates (e.g. car radiator hoses) and hand-built products as rubber coated steel containers.

Steam curing requires a great deal of manual work from one processing stage to another, and this contributes to the high cost of autoclave cured products.
Autoclaves are pressure vessels and need to comply with general regulations for pressure vessels.

Continuous curing of extruded products means that the product, directly after leaving the extruder, continues onwards into a tank or tunnel with a heat-conductive medium.

The methods used include:
Curing in a salt bath
Curing using fluidized beds
Curing with microwaves
Curing using shear extruder heads
Curing using an IR (Infrared Radiation) tunnel

In the first two mentioned methods the extrudate proceeds directly from the extruder into a bath of melted salt alternative of heated glass beads, as the other three methods are based on just heating up the product to curing temperature directly in front of the extruder and then the extrudate pass a heated air tunnel to complete the curing.

The curing temperature in all this methods is normally in the order of 200 °C.
Curing using fluidized beds

Curing in salt bath

Heating up using sheat extruder head
Continuoues curing of calandered products is made in a process called rotocuring in a machine working according to the principle:

The curing drum, a polished steel drum is heated up to a temperature of 160 – 200 °C and the uncured rubber is pressed onto the rotating drum with a steel band. The normal speed range is 5 - 50 m/h depending on the thickness and type of material.

3. 9 Latex processes

As the base material, latex, is fluent, the latex processes differ completely from processing of the solid rubber compounds.

Mixing of solid rubber is a fast process when the time needed for latex mixing technique and maturation is very time consuming and can take 2 to 3 weeks.

The most important manufacturing techniques are:

<table>
<thead>
<tr>
<th>Process</th>
<th>Example of product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dipping</td>
<td>Gloves, balloons, condoms</td>
</tr>
<tr>
<td>Casting</td>
<td>Toys</td>
</tr>
<tr>
<td>Rotational casting</td>
<td>Balls, meteorological balloons</td>
</tr>
<tr>
<td>Extrusion</td>
<td>Thread</td>
</tr>
<tr>
<td>Foaming</td>
<td>Mattresses</td>
</tr>
<tr>
<td>Spreading</td>
<td>Carpet backing</td>
</tr>
</tbody>
</table>
The important products made of latex may be divided into:

Medical products are e.g. medical gloves, anaesthetic bladders, catheters and blood pressure bladders. The global consumption of natural latex products within the medical care products sector is estimated at approximately 200 000 tons per year.

Industrial products are e.g. bellows, protective gloves and isostatic bladders.

Consumer products are e.g. household gloves, toy balloons and condoms

3.10 Urethane rubber

The main part of urethane rubber is processed by casting or by injection moulding of the liquid material. The raw materials a liquid resin, usually a low molecular polyester or polyether, a diisocyanate and one or more hardeners form in a stepwise reaction a cross-linked polymer.

4. Processing in thermoplastic elastomers

The processing of thermoplastic elastomers, TPE is characterized by the fact that the material becomes fluid when heating and then is going back to a solid phase when cooling. Thereby rubber-like products can be manufactured by the use of plastic processing equipment.
The differences between processing of vulcanised rubber and thermoplastic elastomers may be visualized in following way:

5. Facts of processing methods
The choice of different processing methods and the economical view on techniques and qualities aspects are dealt with in this chapter.

6 Environment and recycled rubber
Finally the student will find a chapter dealing with environment matters and the methods of recycling of rubber.

Like all industries, the rubber industry has an impact on the environment. Some of the rubber industries' environmental issues are unique, while other problems are shared by all industries. Unique problems for the rubber industry include the emission of gases, odour and particles from the vulcanisation processes. Problems shared by other industries include noise, waste, emissions to air and occupational safety issues.

After studying this module, the student has obtained a good overview and knowledge of different processing methods used for producing all kinds of products manufactured of
cured rubber or thermoplastic elastomers. The student will also be able to choose a suitable technique that will optimize costs and quality.
The chapter “Rubber Raw Material Testing” describes chemical analyses of raw materials used in the rubber and tyre-making industry. This part is dedicated to a principal explanation of basic determinants in raw material analysis. Such analyses are used primarily to determine basic chemical and physical-chemical constants that are directly related to purity of the used raw materials. The second part describes chemical analyses of vulcanizates.

Rubber Raw Material Testing

Rubber raw material testing usually includes basic chemical-analytical and physical-mechanical measurements resulting mostly in physical constants that can be used to expect purity of the raw materials, such as: determination of melting temperature, contents of moisture, dry matter, ash or volatile substances, determination of viscosity in liquid samples, determination of active ingredient content, determination of heavy metal content (rubber poisons), refraction index, acidity figures etc. Methods used in quality control for input raw materials need to be fast, accurate and their results must correlate with raw material purity.

Vulcanizate Chemical Analysis

More complex procedures are used and instrumental analytical methods are applied in chemical analyses of vulcanizates. This part explains principles of instrumental analyses used in rubber-making practice.

Rubber compound analysis includes the following procedures:
1. Extraction of extractable units from the compound (the extract can contain oils, softeners, fragments of accelerators, antidegradants, waxes, processing admixtures and free sulphur);
2. Determination of sulphur content;
3. Identification of polymer types and their quantification;
4. Determination of carbon black type and content;
5. Identification of inorganic compound ingredients;
6. Identification of accelerators and antidegradants;
1. Determination of Extractable Units

Vulcanizate extraction using a suitable extraction solvent is used to treat a sample before subsequent analyses and to determine content of extractable substances. Several types, mostly of organic solvents (extraction solvents), can be used for extraction depending on the purpose of the analysis.

Acetone extract is used the most often. Acetone extracts resins, free sulphur, acetone-soluble softeners and antioxidants, auxiliary rubber making admixtures, mineral oils, waxes, organic accelerators and products of their decomposition and fatty acids from the vulcanizate sample. It partially extracts bituminous substances, high molecular weight hydrocarbons and soaps. Content of free sulphur, wax and mineral oils can be determined from the acetone extract.

Chloroform extracts bituminous substances and it can be considered to be an indicator of presence of these ingredients in the compound. A chloroform extract contain also additional ingredients including small quantities of rubber. It is applied on a sample pre-extracted with acetone (after determining the acetone content).

2. Determination of Sulphur

Elementary sulphur is used most often in practice as a cross-linking (vulcanization agent). Sulphur is present in vulcanizates after cross-linking (vulcanization) in different forms depending on the acceleration system used and the level of vulcanization. In addition to this, some rubber raw materials contain sulphur in their molecule. Vulcanization is a reaction of sulphur with unsaturated rubber bonds. The sulphur reacts in vulcanization creating various types of sulfidic transverse bonds between rubber chains, but there is also some modification of the chains (bound sulphur). Part of the sulphur, however, stays unchanged and it is referred to as free sulphur. It is usually determined as total sulphur, indicating the total amount of sulphur in the rubber (added sulphur, sulphur coming from raw materials).

Sulphur is determined by multiple methods. All of them are based on oxidation of sulphur atoms to sulphur dioxide or sulphates.

Sulphur is determined by means of an elementary analyser at present. In addition to sulphur, elementary analysers make it possible to determine nitrogen, carbon, hydrogen and oxygen contents. A sample is burnt in the oxygen atmosphere at temperature above 1200 °C, combustion gases are purged and directed into a detector. The most commonly used detectors are either Katharometer detector or infrared detector. Sample masses range from hundredths of milligrams up to approx. one gram; detection limits depend on
sample types and detector types starting from 0.005 mg. The whole analysis takes about 15 minutes.

3. Determination of Polymers

Determination of polymer type and quantity belongs to basic measurements. There are various methods, but instrument methods of chemical analyses are used most often. Polymer determination is also one of the most complex analyses.

Methods based on measurement methods:

Determination of polyisoprene rubber (NR) quantities is based on oxidising a sample with chromium-sulphur mixture. Polyisoprene is oxidised and acetic acid is formed. This acetic acid is determined after distillation by alkalimetric methods using NaOH. The determination is influenced by other polymers present.

Instrumental Determination Methods:

Thermogravimetric analysis:

Thermogravimetry is a method based on monitoring changes in sample mass depending on its temperature. It allows more complex sample analysis, not only estimated presence of certain polymers. A sample is subjected to a controlled thermal programme and its weight is monitored continuously. The following happens when vulcanizates are heated in an inert atmosphere:

volatile units are released up to 150 °C (moisture, volatile organic components…) and volatile softeners (such as oils) start to evaporate above this temperature. Depending on their character (paraffinic, aromatic…), the temperature of the maximum rate of mass change moves either to lower or higher temperatures. In many cases this phenomenon happens simultaneously with the beginning of polymer matrix pyrolysis (pyrolysis of polyisoprene rubber, if any in the sample). This can be eliminated by measuring the sample in the vacuum (lowering the boiling temperature of volatile softeners, such as oils)

Polyisoprene rubber starts to pyrolyse at approx. 370 °C, what can be used for its identification. Butadiene-based rubbers decompose at temperatures above 420 °C because of their lower percentage of unsaturation. Organic substances are decomposed completely at temperature up to approx. 500 °C.

Any present calcium carbonate is decomposed to calcium oxide and carbon dioxide at about 750 °C: \[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \]
carbon black content is determined using their oxidation with oxygen (the atmosphere changes to oxidative). Some organic substances (e.g. compounds containing heteroatom or aromatic hydrocarbons) produce pyrolytic carbon black in pyrolysis, so the set value may be falsely positive for this reason. Analysis conditions can be set to ensure separate burning of pyrolysis carbon black and filler carbon black.

The sample weight at the end of the measurement is given by the amount of the ash.

Infrared spectrometry:

Infrared spectrometry is the most frequently used instrumental method used to identify polymers in vulcanizates. A sample must be extracted before the analysis to remove any softeners that preclude proper identification of polymers. It is extracted using a suitable solvent. The extracted and dried sample is pyrolysed in inert atmosphere. The pyrolysate is collected and applied to KBr tablet and its infrared spectrum is measured. The measured spectrum is compared to spectra of other known polymers and/or with spectra published in the spectra library. A semi-quantitative analysis shall be done on the sample after its dissolution in o-dichlorbenzene and elimination of carbon black by means of colon chromatography. This method is indirect, i.e. a calibration curve must be made with known polymer contents.

Pyrolysis gas chromatography:

The extracted sample is pyrolysed and part of the pyrolysis gases is directed into a gas chromatograph. Specific ingredients are separated and identified in the colon. The most appropriate detection method is to use a mass detector that makes it possible to identify the ingredients on the basis of their mass spectrum in addition to identification on the basis of elution characteristics.

Nuclear magnetic resonance:

Similar to infrared spectrometry, nuclear magnetic resonance is used to identify and determine polymers. In particular, it is used to measure 1H spectra, or 13C spectra in some cases. NMR allows measurements also in the solid phase and possible application of imaging method of selected atoms.

4. Determination of Carbon Black:

Carbon black can be determined by many different methods, such as by organic matrix decomposition using nitric acid, by sample pyrolysis in inert atmosphere or by means of TG.
Decomposition by nitric acid is applicable only for unsaturated rubbers. Nitric acid oxidizes the rubber matrix. Then the sample is filtered, dried and turned to ash in a muffle furnace. The difference in the mass before and after burning is directly proportional to the carbon black content in the sample.

The pyrolysis method is based on a similar principle. The sample is pyrolysed in inert atmosphere, producing carbon black. The carbon black is then burnt in oxidative atmosphere and the carbon black content is determined from the difference in masses. This method is not suitable for samples producing pyrolysis carbon black.

The most appropriate method is TG, as it eliminates formation of pyrolysis carbon black.

Carbon black identification:

Several methods can be used to identify unknown carbon black, though many of them have their limitations. The following methods can be used to identify carbon black:

- Determination of iodine adsorption (the iodine number shows the number of milligrams of iodine adsorbed on the surface of 1 g of carbon black, in common furnace black the iodine number numerically matches their specific surface determined by nitrogen adsorption);
- Determination of cetyl trimethylammonium bromide (CTAB) adsorption – (adsorption of large molecules that cannot enter micro pores, this gives information on the effective external surface accessible for rubber molecules);
- Determination of specific surface area - BET, STSA (based on nitrogen adsorption at a low temperature at which a monomolecule layer is formed. Nitrogen has small molecules, it is chemically inert and its adsorption does not depend on chemical characteristics of carbon black surface);
- Determination of particle size distribution by means of a transmission electron microscope – this provides the best results as regards identification of carbon black used in vulcanizates.

5. Determination of Inorganic Ingredients, Fillers (Ash Analysis)

The term “fillers” refers to the inorganic materials - except sulphur and carbon black - added into a rubber compound.

Considering inorganic ingredients, the contents of heavy metal (rubber poisons), zinc oxide (vulcanization activator) or cobalt (adhesive mixtures), light magnesia, flowers of antimony, lead hemioxide (special thermally resistant compounds especially for conveyor belts) and titanium oxide are determined in particular.

Determination of inorganic ingredients is based on sample mineralization. A sample can be mineralised by various techniques - by dry or wet process, in a closed or opened
system. The most reproducible and most correct results are achieved in a wet closed mineralization. Mineralization is the most critical operation in terms of analysis errors and duration of the analysis.

Metals are determined by atomic absorption spectrometry (AAS), by voltamperometric and/or spectrophotometric techniques of UV/VIS areas. Metals in higher concentrations, such as zinc oxide content, can be determined by measuring methods.

6. Identification of Accelerators and Antidegradants

Commonly used antidegradants and accelerators used in the rubber-making industry are organic compounds. They can be isolated from a vulcanizate by extraction done using a suitable extraction solvent.

The extract contains oils, softeners, fragments of accelerators, antidegradants, processing admixtures and free sulphur. Accelerators can be identified by one of the separation analytical techniques, such as gas chromatography, thin-layer chromatography or highly effective liquid chromatography in combination with a suitable detector. A combination of a separation technique and a detector that identifies analytes by measuring their spectrum (mass, infrared, NMR, such as combinations GC/MS, GC/FTIR, GC/NMR or HPLC/MS, HPLC/FTIR, HPLC/NMR) is very effective. Most accelerators decompose by vulcanization, so it is useful to identify them from presence of reaction products (e.g. cyclohexylamine to be identified is formed from N-cyclohexyl-2-benzthiazolsulphene amide (CBS).

7. Identification of Stiffening Materials

A tyre is a composite product. It contains various types of stiffening materials in addition to rubber. The most common are stiffening fabrics and steel stiffening materials (used in the form of tyre cords or fabrics).

Infrared spectrometry is the most frequent method used to identify stiffening materials. A sample is dissolved in a suitable solvent and analysed by a proper technique (e.g. KBr tablet).

A stiffening material can be identified also from its melting temperature. The melting temperature is determined by measuring a DSC record.

The original vulcanizate formula can be “reconstructed” on the basis of results from chemical analyses. Analytical techniques can be used to address problems of new product development, to analyse their properties and similar.
The chapter named “Rubber Compound and Vulcanizate Testing” is related to the chapter on “Rubber Raw Material Testing” and provides a comprehensive description of the system of testing rubber compounds, materials and vulcanizates, starting from sampling and testing vessels up to evaluation of test results according to specific standards.

The chapter is divided into four parts as follows:

- Rubber Compound Testing
- Testing Rheologic Properties of Compounds
- Vulcanizate Testing
- Dynamical-Mechanical-Thermal Analysis of Vulcanizates

explaining in detail specific testing procedures and methods arising from national and international standards or expert literature specialising in this field.

**Rubber Compound Testing**

This includes two fundamental testing methods – determination of viscosity and scorch and determination of vulcanization characteristics.

**Determination of Viscosity and Scorch**

Viscosity (in older literature referred to as plasticity – this property is indirectly proportional to viscosity) is a typical property of rubber and depends on molecular mass and its distribution. **Viscosity characterises workability of rubber**, i.e. possibilities of processing it by mechanical means. The Mooney viscosity is used most often in practice. Viscosity of rubbers or rubber compounds depends on their temperature.

Viscosity is determined on the basis of torque measurements for a shear disk placed in a sample inserted into a heated chamber of the apparatus. The Mooney disk viscosimeter is used in the test. In addition to Mooney viscosity, other compound characteristics can be evaluated, such as Delta Mooney, scorching and relaxation.

**Determination of Vulcanization Characteristics**

Vulcanization curves are an objective and representative means of expressing the course of vulcanization. They make it possible to set optimum technological conditions in production and to control the compound accurately. They are also a realistic ground to study the mechanism of vulcanization.

Special apparatus is used to determine them - the so called vulcameters that record the entire vulcanization curve automatically from a single sample of the compound.
A kinetic curve (the term **vulcanization curve** is used in rubber industry) is a **graphic representation** of the chemical reactions described above. The curve is used to identify vulcanization characteristics of the rubber compound, such as \( t_{10}, t_{90}, M_{\text{max}}, M_{\text{min}}, \) etc. The vulcanization curve can be used to calculate even the vulcanization speed constant; vulcanization activation energy can be calculated from vulcanization curves measured at various temperatures.

Vulcanization characteristics are measured using an apparatus called a vulcameter or rheometer. Older apparatuses contain a bi-conical rotor in the heating chamber; newer apparatuses have no rotor. The best known apparatuses are MDR 2000 (Moving Die Rheometer) made by Alpha Technologies, previously Monsanto.

**Testing Rheologic Properties of Compounds**

**Rheology** can be defined in general as **a study of deformation and flow of matter.** As regards rubber compounds, only solid and liquid state and transition areas between them typical for macromolecular substances are worth discussing.

The aim of rheology is to provide a detailed characteristics (using a mathematical model) of a non-ideal behaviour of polymer liquids. Viscosity is the basic flow property. It is a function of both temperature and shear speed and of polymer’s macromolecular characteristics (molecular mass, molecular mass distribution, structure of monomere unit), but also of additive concentration (such as the level of filling) and other factors (pressure…).

The so-called flow curve is a mathematical expression of flow properties. It represents a function dependence of shear rate \( \gamma \) and shearing stress \( \sigma \) (sometimes referred to as „\( \tau " \)). The simplest and most frequently used mathematical expression (the so-called rheological model) for purely viscous liquids is the Power Law:

\[
\sigma = K \cdot \dot{\gamma}^n
\]

This model contains two parameters, where \( K \) is the consistency coefficient and \( n \) is the index describing the degree of deviation from the Newtonian behaviour.

Viscosity of polymer melts is influenced by several factors. Viscosity of a melt is influenced the most by temperature, pressure, molecular characteristics, amount of filler added, polymer chain structure, addition of auxiliary manufacturing admixtures.

It is temperature that influences flow properties of polymer melts the most. A melt viscosity changes significantly with changing temperatures of polymer processing. In temperature intervals significantly exceeding the vitrification transition temperature \( T_g \), viscosity can be defined as a function of temperature using a modified Arrhenius relationship:
\[ \eta = B \cdot e^{\frac{E_a}{RT}} \]

where B is a constant and characterises the polymer and its molecular mass, Ea is the activation energy of the polymer melt flow.

**Rheometry** is a broad branch of science **studying rheologic properties of substances**. Generally it includes rheometric methods, methodologies and apparatuses used for measurements - rheometers.

The equipment used to measure rheologic properties of rubber compounds can be divided into the following categories according to their principle:

- Rotational rheometers;
- Oscillation rheometers;
- Capillary rheometers;
- Flow rheometers.

**Rotational rheometers** are based on the principle of measuring resistance of the environment against turning of a body of an exactly defined shape with a circular speed \( \omega \). The degree of resistance of the environment against the turning is given by the torque \( M_t \), directly proportional to the shearing stress. Angular speed \( \omega \) is independently variable and directly proportional to the shear rate. A typical example of the apparatus is the Mooney viscosimeter, Monsanto vulcameter.

**Oscillation (rotorless) rheometers** – these apparatuses commonly used to measure flow properties, include MDR 2000 and RPA 2000 rheometers. The difference between the two apparatuses is that the oscillation frequency and amplitude may not be modified during a measurement using a MDR apparatus, but new processing technologies require a better knowledge of rheologic properties of compounds. A RPA 2000 (Rubber Process Analyzer) apparatus allows a modification of amplitude (between \( \pm 0.02 \) and \( \pm 90^\circ \)), frequency (between 0.033 Hz and 33 Hz) and temperature (between 40 °C and 200 °C). RPA 2000 allows you to measure viscosity and elasticity characteristics of raw, vulcanised and pre-vulcanised mixtures.

**Capillary rheometers** are based on the principle of measuring the flow of the melt by influence of a pressure exerted by a capillary of exactly defined dimensions. Testing equipment used in capillary rheometry include capillary rheometers in particular. Proper capillary rheometers to determine characteristics of rubber compounds are laboratory threaded devices (marketed by several companies, such as Thermo Haake or Brabender).

**Vulcanizate Testing**

This includes determining physical and mechanical properties, aging tests and dynamic tests.
The main **physical and mechanical properties of vulcanizates** include density, stress-strain properties (strength, elongation, modulus), hardness, rebound resilience, tear strength.

**Stress-Strain Tests**

They provide a basic overview of properties of a rubber material. They are also used to check regularity of technological properties, such as quality of mixing the rubber compound. The dependence of stress on elongation is typical for every rubber compound. The so-called tensile curve is a mathematical expression of this dependency. The maximum stress and strain can be determined from the curve as well as the stress needed for a specific elongation – a module used very often as a measure for evaluating elastic properties of the rubber. This module is not identical with Young's elastic modulus specifying the stress needed for the initial length to double.

A close look at the graphic record of dependency of the stress on elongation will show that this dependency is linear only with small stress (it follows Hook’ law of elasticity), then it follows a more or less arched curve and increases sharply at the end when rubber solidification occurs and it increases up to the final destruction of the sample.

Stress-strain tests are done by tensile testing machines with a suitable stress range. Various types of testing bodies are used in tests. Testing bodies in shape of bilateral blades or sometimes in shape of a ring are used most often.

The testing bodies are prepared by cutting them out with a suitable cutting knife from a vulcanized disk or ring.

The test is done with defined deformation rate and at constant temperature. The value of the stress is monitored by a suitable sensor; elongation is usually measured by a touch or optical extension meter or by a video extension meter.

**Hardness Measurement**

This is based on measuring the penetration depth of a tip of defined size into the material. In a cylinder intendor, the indentation value is directly proportional to the stress and indirectly proportional to its diameter.

Various types of hardness testers are used to test rubber hardness. The principle of their function is to measure the depth of penetration of a measuring body into the sample. Various hardness testers differ mostly in shape and size of the testing tip, size of the stress and nature of its application, as well as in the way how results are presented. The Shore A method is the most common in hardness measurement.
Determination of Rebound Resilience

This belongs to the best known methods used to determine ability of rubber to absorb mechanical energy upon impact. The measurement is based on measuring the height of rebound of a metal pendulum from the testing body. Two methods are based on this principle: the Schobe and Lüpke methods. The value of rebound resilience depends on thickness of the testing body. Temperature and surface of the testing body have a significant influence on the rebound resilience value.

Determination of Tear Strength

These ranks to structural tests together with determination of rub resistance. It is determined from a tensile stress applied to a suitable testing body. It is very important to select a suitable testing body, because in an improperly selected shape and size of the testing body, the value of tear force shows tensile strength instead of tear strength (the strength needed to tear the vulcanizate structure).

The following types of testing bodies are used: crescent (without score), graves (with or without score), trousers.

Tests are done by tensile testing machines in a way similar to determination of stress-strain properties. The result is expressed as the force needed to tear a sample with a specific thickness in kN.m$^{-1}$.

Determination of Rub Resistance

This is important especially for those products that are subjected to a friction stress during use (such as treads, cover layers of conveyor belts). Product life can be predicted on the basis of the rub resistance level.

The methodology (Bussen-Schlobach methodology) of the test involves a testing body in the shape of a cylinder is rubbed on a cylinder with surface covered by a rubbing agent. The testing body is re-grinded before the test, its weight is measured and it is rubbed on a rotating cylinder with a rubbing component. A mass reduction is determined after covering 40 m of the trajectory and a relative decrease in volume shall of $\Delta V$ be calculated.
Aging Tests

Various, especially chemical changes, occur in the rubber due to different external factors and they result in a shorter product life. These changes can be summarised as aging. The main factors causing reduced lifecycle of the material is the air oxygen, ozone, higher temperature and electromagnetic radiation. These factors have a common influence during product exploitation. Determining these influences in natural conditions is very time consuming the obtained results are not repeatable. This was the reason for developing accelerated aging test in which test conditions are modified to have only one of the aforesaid factors at one time or the factors may combine.

Determination of Accelerated Thermal Aging in the Air

This method is based on comparison of physical and mechanical properties of the testing bodies exposed in an anon-deformed state to hot circulating air for a period of time in a thermostat (method A) or in test tubes (method B) with properties of testing bodies that were not exposed to the elevated temperatures. Resistance to accelerated thermal aging in the air is determined using a set of physical and mechanical properties, which are important in practical application of the product. Unless there is a defined set of properties, it is recommended to determine them as follows: Tensile strength, module at a specific elongation, extension and hardness. A testing apparatus for method A makes use of a thermostat with forced air circulation. In method B, test tubes inserted in a heated metal block or in liquid baths with air exchange as in method A.

Determination of Accelerated Thermal Aging in Oxygen

The principle and procedure of this method is identical with the preceding method, the only difference is in usage of a different testing apparatus consisting of an oxygen chamber and a thermostat.

Determination of Resistance to Ozone Exposure

Testing bodies are exposed to a static tensile stress in a closed chamber at constant temperature in an atmosphere containing a set ozone concentration. The testing bodies are checked on a regular basis whether there are no cracks formed on their surface. The testing bodies are made in the form of strips or bilateral blades and their surface may not be damaged (grinded, cut, etc). The test is done with one of the following ozone concentrations: 25 pphm, 50 pphm, 100 pphm, 200 pphm. The temperature of 40 °C is preferred during the test, but other temperatures may be used, too, such as 23 °C. The test are usually done at one or several strain values (tensile deformation): 5%, 10%, 15%, 20%, 25%, 30%, 40%, 50%, 60%, 80%.
Another method of evaluating resistance to ozone is a test determining rubber resistance to ozone by means of a threshold deformation on testing bodies in the shape of a trapezium.

**Determination of Effect of Liquids**

A typical feature of rubber materials is their very low resistance to solvents, especially organic ones. Non-vulcanized rubber dissolves well in organic solvents, but this property disappears with rubber vulcanization (cross-linking). A vulcanizate only buds in solvents. To determine resistance to liquids it is necessary to select a proper test temperature and a proper degree of air access. Considering the fact that the penetration rate of liquid into rubber depends on several factors, it is not possible to choose only one time interval for the test.

A percentage of change in volume or mass is determined.

Changes in physical properties after exposure to liquids can be determined immediately after the exposure to the tested liquid or after its elimination or after the liquid dries. A change in tensile properties and hardness is evaluated, as well as other physical and mechanical properties in specific cases.

**Determining a Permanent Tensile Strain**

The aim of the test is to determine a value of a permanent tensile strain of a vulcanizate to describe the viscous component of the viscous-elastic rubber behaviour. It is used to evaluate suitability of using the rubber product, such as tyres, membranes, gloves. The value of permanent strain shall be calculated.

**Determining a Permanent Compression Strain**

The test procedure is similar as in determination of a permanent tensile strain; the only difference is in the shape of the testing body used. Testing bodies in the shape of a small cylinder, type A and B can be used. The size of the strain is selected according to rubber hardness from 10 % to 25 %. The calculation is similar to the one in permanent tensile strain.

**Determining Limits of Cold Flex Temperature**

The basis of the method is to determine the temperature at which a testing body remains intact. This value shall be used to determine approximate thermal limits for using the product at low temperatures.
Dynamic Tests

Many rubber products undergo a dynamic stress during exploitation. Considering this, suitability of using a rubber compound in a car tyre is given by knowledge of its dynamic properties. These tests are suitable especially for dynamically stressed compounds, e.g. in car tyre sidewalls.

Determination of Resistance to Formation and Development of Cracks by Flex Cracking

The test is based on repeated flexing of the testing body at a constant frequency, during which a change in the surface is monitored (formation of a crack at the narrowed point of the pattern) or size of a crack made artificially before the test (initial crack 2 mm wide) depending on the number of flexions.

Determination of Resistance to Fatigue and Temperature Increase using a DPGi Apparatus

The testing body in the shape of a small cylinder is fitted into rotating jaws of the DPGi machine and the required flexion angle is set by shifting the fitting unit. The testing body rotates at frequency of 15 Hz. To determine resistance to fatigue, the body is left to rotate until it is destructed and the number of rotations made is read. Material heating is determined by measuring the internal sample temperature using a suitable sensor after completing a set number of rotations.

Adhesion Tests

A tyre casing is a composite material. This means that it is made of various construction materials, such as rubber compounds, steel cord materials and fabric stiffeners. In terms of safety of driving and tyre life, it is essential to ensure their maximum compactness so that specific layers of these stiffening materials do not separate from each other. Stiffening material adhesion can be evaluated by static and dynamic methods and they are decisive for the so-called adhesive compounds. Basically, every adhesion evaluation method measures the force needed to separate a stiffening material from the rubber at set conditions. The differences can occur in sample treatment, experiment arrangement or conditions of measurement. The most common measurements include: determining rubber-metal cohesion, determining cohesion between layers after separation, determining static adhesion of rubber and fabric cord (H-test) and determining cohesion after dynamic deformation using the Henley method.
Dynamical-Mechanical-Thermal Analysis

The dynamical-mechanical analysis can be described simply as application of an oscillation force on the sample and analysis of response of the material to such force. This is used to calculate properties such as proneness to flow (called viscosity) from a phase shift and stiffness (modulus) from sample restoration.

The basic quantities measured in a DMA analysis are force and changes in dimensions of the tested material. These quantities can be used to calculate nodule values, whereas a type of the modulus depends on a type of dynamical stress (i.e. shearing stress, tensile stress, bending stress, pressure stress etc.) and on the viscosity value that indicates the resistance of the material to flowing.

One of the advantages of DMA is that you can get a modulus anytime and the application of the sinusoid provides analysis along the whole range of temperatures, frequencies, deformation and time.

One of the examples of using DMA to explore material properties is to establish a graphic dependency of the elasticity modulus on temperatures, where you can see changes in the modulus at low temperatures. This shift is referred to as a vitrification shift ($T_g$) or an alpha-shift ($T_\alpha$).

Just like using DMA for a fast mapping of the material modulus depending on temperature, DMA can be used for a prompt evaluation of effects of shear rate or frequency on viscosity.

Finally, many types of DMA offered on the market enables creep and relaxation testing. A creep (flowing) is one of the fundamental tests of material behaviour and it is directly applicable to resultant properties of a product. A creep-relaxation test is also a very powerful analytical tool. These experiments make it possible to determine a response of the material to constant stress and its behaviour once this stress is removed.

The chapter named “Laboratory Tyre Testing” discusses tyre testing in laboratory conditions. The advantage of these tests is their high repeatability and reproducibility given by the possibility to control test conditions and parameters very precisely. Depending on the nature of the test, these parameters include speed, radial stress, inflation pressure, angle of deflection, angle of directional deviation, ambient temperature, relative humidity of the environment and duration of specific test steps. Laboratory tyre testing can be classified according to multiple aspects. One of the classification methods is to divide them according to the purpose of use for specific vehicle categories:
- Tyre testing for passenger vehicles;
- Tyre testing for utility vehicles;
- Tyre testing for agricultural vehicles and forest tractors, multi-purpose vehicles, earth machines and special vehicles;
- Tests of tyres, solid casings and tyres for industrial trolleys, handlers, carts etc.

As regard tyre nature, tyre tests can be divided as follows depending on the condition of a tested tyre:
- Static tests and measurements – the tyre does not roll and rotate and its properties are measured in a static state;
- Dynamic tests – these tests are based on a simulation of tyre rolling on a testing machine with a drum, usually in the shape of a cylinder with defined surface in order to determine endurance of a tyre casing;
- Special dynamic measurements - their aim is to determine various properties of a rotating tyre that affect behaviour of a vehicle in operation.

**Preparation of Tyres for Laboratory Tests**

Before assembly onto disk wheels, casings, tubes and flaps undergo a visual inspection in order to detect visible defects. Tyre casings can be subjected to non-destructive analyses and tests (X-ray, ultrasound, holography, interferometry, test uniformity) before the tests. Casings are treated at room temperature before assembly, only then they can be assembled to the rim (potentially with the tube and the protective flap) and the relevant test methodology can be followed. When fitting the casing onto a test rim be careful to avoid damage to the casing, tube or flap. Some tests require tyre stabilisation by running-in on a drum testing machine. This ensures stability of certain properties and eliminates mechanical tensions present in the casing when it is pressed.

**Static Measurements**

Static measurements determine properties and characteristics of non-rotating casings and tyres. Static measurements include in particular the following:
- Measurement of tyre casing mass;
- Measurement of tyre crest thickness;
- Measurement of tread hardness;
- Measurement of basic external tyre dimensions;
- Measurement of static radial stiffness;
- Measurement and analysis of tyre footprint;
- Measurement of contact pressure distribution in tyre footprint;
- Measurement of strength by fracture in the crest;
- Determination of casing resistance to destruction by water pressure;
• Measurement of resistance of a tubeless casing tyre bead against slipping from the rim;
• Measurement of pattern depth and height of wear indicators;
• Measurement of contact forces in the tyre bead;
• Measurement of tyre air-tightness;
• Measurement of surface electric resistance.

Casing mass is measured in two ways – either by determination of masses of specific components or by measuring casing in series containing several pieces. Casings are weighted on platform scales; smaller casings can be weighted on suspension scales with an electronic load gauge.

Some manufacturers use measurement of tyre crest thickness to check quality of serial production of both new and renovated (re-treaded) tyres. The measuring device consists of a calliper and a support bead the tyre is placed onto so that the support bead is in the middle of the tyre crest from the side of the inner rubber. The middle of the crest is then pushed onto the calliper from above and the tyre crest thickness is measured.

Tread hardness is measured using a Shore hardness tester and it is expressed in Shore units. Its importance can be seen in comparisons of various casings and tread compounds as well as in quality assurance in tyre re-treading by the so-called warm method, i.e. by application of a new material followed by vulcanization. Tread hardness is measured in the middle of a pattern figure. The hardness value is read after 3 seconds from placement of the tester on the pattern figure. The value of hardness depends on temperature of tyre tread; therefore it is necessary to treat the tyre at room temperature before taking the measurement.

External tyre dimensions are measured on a tyre consisting of a tubeless casing, rim and valve or from a casing with a tube, flap and a rim. Inflation pressure and width of the rim used have a great influence on resultant values when basic external dimension of tyres, forming the total width and external diameter, are measured. During the test, a tyre inflated to a relevant pressure will be treated for at least 24 hours. The total width is measured by a calliper at six points distributed evenly along the tyre circumference. When measuring the total tyre width, this dimension includes any protrusions resulting from casing description, decoration or a protective strip over the bead. When measuring the tyre profile width, measure the smallest linear distance between external borders of a sidewall of an inflated tyre and do not take into account any protrusions resulting from casing description, decoration or a protective strip over the bead. The resultant value is the highest of the six measured values, or seldom the arithmetic average of these values. Tyre circumference is measured by a steel band chain in the middle of the tyre crest with accuracy to 1 mm. The external tyre diameter is calculated by dividing the tyre circumference by $\pi$ (conventionally 3.1416).
The method of determining static radial stiffness is based on measurement of deformation of an inflated tyre depending on the size of a radial stress on the tyre. The test is done by means of a test device consisting of the bearing part with a shaft and the inflated tyre to be tested is mounted on this shaft. The second basic part is a measuring table with a support flat pad parallel to the axis of tyre rotation. Radial stress and radial strain are recorded during the test. Before stressing the tyre, a free tyre circumference is measured using a steel band chain and this value will be used to calculate a static radius. The tyre is the pressed on the measuring table at prescribed speed. Tyre deformation is recorded from the moment of the contact of the casing with the measuring table until a radial stress of 150 % of the maximum tyre capacity is reached. It is measured at least at four different places on the tyre distributed evenly along the casing circumference. Arithmetic average and static radial stiffness \( C_r \) of the tyre in kN.mm\(^{-1}\), as well as tyre static radius \( r_s \) will be calculated from the measured dependences of radial strain at stress equivalent to 75, 100 and 125 % of the maximum permissible tyre capacity. In addition to static radial stiffness, it is possible to measure static lateral, circumferential and torsion stiffness providing information on tyre stiffness in every direction.

Static tyre footprint is evaluated from an imprint prepared by means of the same stressing device that was used to measure static radial stiffness. A tyre consisting of a casing mounted on a prescribed rim and possibly with a tube is inflated to the prescribed pressure and pressed radially to a hard paper (drawing) on the measuring table. Before pressing the tyre, apply a stamping colour or ink on the area of the casing tread that will come into contact with the paper and that makes the tyre footprint. The contact time depends on specific test methodology. The tyre can be released immediately after the maximum set stress is reached, or it can stay under this stress for some time before it is released. Imprint of the tyre footprint will be scanned when it is dry. Dimensions of the footprint and solidity of the pattern will be evaluated, i.e. the ratio of the contact surface to the total surface of the imprint.

Contact pressure distribution in tyre footprint is measured either electronically or optically. In the electronic method, the tyre is pressed to a special board made with contact pressure sensors that will record the pressure in the whole footprint. This method is favourable as it requires no consumables. The possibility to monitor contact pressure at specific points of measurement depending on time is yet another advantage. Its disadvantage is the high price of sensor boards and a higher span between sensory points compared to optical methods. Optical methods are based on usage of a special pressure-sensitive foil with microgranulated colour-generating material to be inserted between a solid pad and the tyre. As pressure is applied, the micro granules disrupt and the colour-generating material reacts with a development material generating a colour. The microgranules are designed to react according to the degree of pressure so their colour corresponds to the degree of the pressure. After this stress, the foils are evaluated by means of reading devices or by means of a scanner with specialised software that enables a complete analysis of the imprint. The disadvantage of this method is that the foil
records only the maximum pressure exerted and this pressure is evaluated only after it is not applied any more, so it is not possible to monitor changes in the contact pressure in time and the values cannot be recorded on-line.

One of the methods used to determine strength of the casing is the **fracture in the crest** test. In this test, a rounded mandrel of prescribed shape and size is pressed into the middle of the crest of an inflated and fitted tyre. The purpose of the test is to assess strength of stiffening materials used. The mandrel should be placed as close to the plane of symmetry in the tyre to have the test point in the middle of the pattern figure. The measurement is done at five points distributed fairly evenly along the casing circumference. A criterion to end the test is either a fracture of the casing, achievement of the desired value of deforming work (fracture energy) or a contact of the inner rubber with the rim. The result of the test is the fracture energy calculated as an arithmetic average from respective measurements of the mandrel force and penetration.

A second test to determine casing strength is a **water pressure** test. This method is based on determining strength of a casing stressed by the pressure of the water filled into the tyre. In this test the casings are mounted either to reinforced disk wheels or to a special device with segments and a contact surface in the shape of a rim. A deflated tyre is filled with water until the casing is destroyed. The result of the test is the nature, point and extent of casing disruption, pressure and possibly increase in internal tyre volume at the time of casing destruction.

Measurements used to assess safety of tubeless casings include a determination of **resistance of a casing tyre bead against slipping from the rim**, what is a reaction to an applied lateral force. The result of the test is the lowest stress force at which the tyre bead shifts at the rim contact surface, resulting in air leakage from the tyre. Resistance of the tyre bead against slipping from the rim due to excessive lateral force can be induced in a laboratory by progressive pressure of a stress force applied on the bead and this force is applied by means of a segment of adjusted shape until the tyre bead slips from the rim and a fast air leakage occurs. The test is repeated at least at four points fairly evenly distributed along the casing circumference and the magnitude of the force at which the bead slips from the rim is recorded.

**Depth of pattern grooves and height of wear indicators** is measured to evaluate patterns on new and renovated casings, to evaluate casing resistance to wear and to assess condition of the casing. Pattern groove depth is measured at least at six points evenly distributed along the casing circumference so that the depth meter tip is perpendicular to the running surface of the tread. It is measured close to the wear indicators in the main pattern grooves. To measure height of wear indicators, first measure the depth of the pattern groove in close vicinity to the wear indicator at its footing and then measure the pattern groove depth directly on the indicator. The difference between these values gives the height of the wear indicator.
Measurement of **contact forces in the tyre bead** is intended to determine radial stiffness of tyre bead. The test is done using a device with jaws consisting of specific segments that expand by means of hydraulic cylinders. Every segment pair has a load gauge in front of it to measure the force applied by the segment on the tyre bead and vice versa. In addition to this, the device must be equipped with a segment position sensor against a zero position, corresponding to the nominal rim diameter \(D_{\text{nom}}\). The casing is placed on the jaws with its serial side. The jaws are completely retracted to the minimum diameter in their baseline position to allow placement of the tyre bead. When the load gauges are zeroed, the jaws are expanded to diameter of \(D_{\text{nom}}+0.8\) mm to ensure pre-stress of the tyre bead before the measurement; afterwards the jaws return into their baseline position. Value of the bead radial stiffness is determined by re-expanding the jaws at values of tyre bead deformation of \(D_{\text{nom}}-0.29\) mm for the safety limit and \(D_{\text{nom}}+0.38\) mm for the mounting limit. Then use the same procedure to measure the bead on the opposite side of the casing.

**Air-tightness of tubeless tyres** is evaluated by determining the decrease in air pressure in the tyre by two ways - either by measuring air-tightness by submerging the tyre in water or by a direct measurement of air decrease using a manometer. For the second method, the test takes 28 days during which the tyre is placed in a conditioned room. After this time, decrease in air pressure in the tyre is measured using a manometer.

**Measurement of surface electric resistance in casings** is very important, especially for vehicles intended for transportation of flammable and explosive substances. Surface electric resistance is measured on a clean and dry casing. An ohmmeter for measuring insulation resistance with special electrodes and range of at least \(10^{10} \Omega\) is used for this measurement. It is important to respect measurement conditions, especially the relative moisture of surrounding air, as this can significantly affect measurements of surface electric resistance. Electric surface resistance is measured at five points with special circular electrodes between the centre of the tread and the point on the sidewall where the casing contacts the rim. Another method is to measure electric surface resistance of a stressed tyre, where an insulated conductive board is placed between the tyre and the ground and electric resistance between this board and the wheel disk is measured.

**Dynamic Tests**

The term dynamic test refers to the tests in which the tyre rolls on a steel drum of the testing machine until the casing is destroyed to determine tyre durability. These tests include speed tests and endurance tests.

**Speed tests** are used to verify durability characteristics of casings by rolling them on the external or internal surface of a testing drum, preserving prescribed requirements for speed, radial stress, inflation, ambient temperature, deflection, directional deviation,
acceleration, braking and duration of specific test steps. Duration of dynamic tests is given either by prescribed time or by disruption in casing structure and integrity. Speed tests for casings on passenger cars focus on verification of casing durability at high speeds that come near or exceed the speed category of the casing. A typical disruption of the casing during speed tests are pieces of rubber thrust out of the pattern, pattern figures torn out and separated stiffener belts (impact plies). Speed tests are based on the principle of progressively increasing speed of the drum with constant radial stress in prescribed increments of time until the prescribed time is reached or the casing is destroyed. The pressure in the tyre is not adapted during speed tests and a constant radial stress is maintained. The tests can be done also with a non-zero tyre deflection, which is usually 4°. Since separated stiffener belts and/or torn out pattern figures are a typical disruption of the casing during high speed tests, the casing is subjected to a higher stress on the side adjacent to the drum in tests with deflection.

Endurance tyre tests are dynamic tests carried out to determine durability of tyre casings. These tests take much more time than speed tests. Endurance tests are usually done at a constant speed. Other test parameters, such as radial stress and inflation, can be but need not be constant during the test. Test conditions are chosen according to the part of the casing the test should focus on. There is no universal endurance test. Endurance tests usually focus of tyre beads and framework area, and on stiffener belts in particular. Tyre endurance tests can be carried out in test rooms with temperatures of (25±5) °C or (38±3) °C.

Special Dynamic Measurements

Special laboratory dynamic measurements of tyres refer to tests in which the tyre rolls on the surface of a drum or a running flat steel belt of a testing machine and various tyre properties and characteristics manifested during exploitation of the tyre are measured during such tests. Important dynamic measurements include measurement of rolling resistance, measurement of dynamic directional characteristics, measurement of tyre properties in a high speed uniformity test, tyre noise measurement and measurement of heat distribution on casing surface. An important feature of special dynamic measurements is that there is damage inflicted to the tyre casing and the tyre can undergo other measurements and tests.

In rolling resistance measurement it is necessary to measure small forces in presence of much bigger forces and this requires usage of equipment with relevant accuracy. The rolling resistance coefficient \( C_r \) is used to indicate rolling resistance. The coefficient is calculated as a proportion of rolling resistance in N and tyre radial stress in N. The tyre rolling resistance is then measured using a force, torque, performance or inertia method. Rolling resistance is measured by means of testing machines with a cylindrical drum with
diameter between 1 500 and 3 000 mm. In force method, the reaction force on the tyre shaft is measured and passive losses caused by shaft friction and aerodynamic resistance of the tyre are deducted from this force. In torque method, the driving torque of the test drum with the tyre with a set radial stress and the passive torque are measured. The performance method measures electrical quantities related to motion of the testing machine drum; the inertia method measures the time needed to stop a tyre pressed to the drum and running down freely. The resultant measured values of rolling resistance are adapted to temperature of 25 °C in every category.

**Dynamic directional characteristics** measure lateral force and a restoring moment of the tyre rolling on the surface of the testing drum at a constant speed. Dependency of the lateral force or of the restoring moment on the angle of directional deviation will be used to determine directional stiffness and restoring moment stiffness respectively. Dynamic directional characteristics are very informative as regards tyre behaviour in controlled vehicle axles, where these characteristics determine behaviour of the tyres associated with a transfer of lateral forces at given direction of the steering wheel and the related angle of directional deviation of the wheels. Lateral force and the restoring moment are measured by means of the so-called multi-component heads. These are special cartridges disk wheels are mounted onto and they have a set of tensometers and piezoelectric sensors that can measure – after amplification using a measuring amplifier - specific parts of forces and moments exerted onto the tyre.

**The high-speed uniformity test** is done additionally to a common casing uniformity test using testing machines structurally similar to those used for high-speed tests. The basic part of the machine is a drum fitted and driven in the base framework, with diameter of 1 500 to 3 000 mm and with smooth surface, together with a tyre stress system. The framework is sufficiently tough and it has high frequencies of its own, ensuring that there will be no resonance in the system during measurements of a tyre rotating at high speeds. Properties similar to a common uniformity test are measured during a high speed uniformity test. However, centrifugal forces are exerted on the tyre at high speeds and tyre behaviour resembles the behaviour under real conditions in the vehicle.

Touch-free optical measurement is used in practice to measure heat distribution on casing surface. This measurement uses cameras sensitive to radiation in the infrared field, which are able to measure temperature of rotating bodies. A signal from such camera is processed in a computer, casing surface is displayed and a certain image colour is allocated to every temperature interval. In addition to quality control of a product under development, measurements of temperature of rotting tyres are important to verify a dynamic-mathematical module of the tyre.

**Casing deformation in dynamic state** is measured for needs of research and development. This can be measured by optical methods based on triangulation, measuring shifts of the object in a dynamic scheme. A tyre is rolling on a rotating drum;
it is stressed by a selected radial stress and inflated to a desired inflation pressure. Measurement points must be applied on the casing surface, making up a black-and-white contrast pattern. Once the casing is recorded by cameras in several states, the system will use the black-and-white structure to find the relevant measurement points to calculate shifts and deformations against the reference state, being the static state this case. Other pictures are acquired at set speeds as needed depending on the speed category of the tested casing. Output parameters include shifts in all three orthogonal directions and deformation at the given rolling speed.

The chapter named “**Tyre Testing in Real Conditions**” discusses the term of “real testing conditions”. What is important that all the tests are carried out on common vehicles by experienced skilled and trained drivers.

The tests are done for two types of vehicle behaviour on the road:
- Standard
- Extreme

Testing surface types are the most important test requirements and they include:
- Dry roadway
- Wet roadway
- Snow compressed by cars
- Ice (flat, clear)

Vehicle tyre tests are divided into the following groups according to testing methodologies:
- Wearing test (life tests)
- Tests on a test track, also referred to as special tests

The special tests are divided into the following groups depending on their nature:
- Subjective
- Objective

Tyre preparation before the tests is very important - tyres need to be mounted on the rim, properly inflated, balanced or run-in.

**1. Wearing Tests (Life Tests)**

Tyre life is the mileage driven by a vehicle before the pattern depth decreases under a set limit.
A vehicle drives test road tracks and when it completes a regularly repeated path the groove depth will be measured on every casing tread in the vehicle. Depth of every
groove is given by the lowest value from depth measurements along the whole circumference of the relevant groove. All the groove depth measurements are then evaluated using a PC.

2. Special Tests

2.1 Subjective Tests

There are drivers selected for this purpose, who can manoeuvre a vehicle in extreme situations at the limit of tyre capacity and to make a very precise subjective evaluation of tyre behaviour. Tyres are evaluated in terms of driving properties, noise emitted by tyres rolling on the roadways and comfort of driving, i.e. the degree of pleasure of controlling a vehicle equipped with respective tyres.

The subjective assessment takes into account:
- Driving properties (behaviour of the car with a certain driving method) – zero position, response, sensitivity to ruts in the road, changed stress in a turn, limit range of control
- Tyre noise – on various road surfaces
- Comfort of driving – silencing impacts, vibrations, influence of the road on driving

A 10-point scale is used in the evaluation, where 10 is the ideal grade for the property to be assessed. The drivers accompany the evaluation with their verbal opinion.

2.2 Objective Tests

These are the tests that focus on specific properties measured by measuring apparatuses placed on the vehicle or outside. The tests are done by comparisons. This means that properties of the so-called reference tyres, expected to satisfy certain operation criteria and deemed to be good-quality tyres, are measured before measuring properties of the casings to be tested. Reference tyres are usually tyres manufactured by leading foreign producers.

- Braking track – the distance needed to stop a vehicle at a certain speed.
- Manoeuvrability – measuring the time needed to complete a road track made of various types of sections
- Slalom test - measuring the time needed to drive through a section with traffic cones
- Overtaking manoeuvre – passing by an unexpected obstacle
- Coasting – the distance travelled over a flat section without motor drive
- Noise measurement in the vehicle – noise level emitted by the tyres as they roll on the roadway
- Effective rolled circumference – the distance covered by one rotation of the wheel
Reinforcing materials in Rubber Products
Virtual Education in Rubber Technology (VERT), FI-04-B-F-PP-160531

SUMMARY

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Many elastomer types are too weak to be used without some reinforcing system. This means that most practical rubber products include the concept of reinforcing the elastomer matrix with some reinforcing agent.

There are two main possible reinforcing principles: either the elastomer matrix is compounded with reinforcing fillers or the product is provided with some fibre consisting components applied in the product assembly phase.

The primary function of a reinforcing filler is to improve the mechanical properties of the rubber compound, whereas the fibre based components have the extra purpose to give adequate functional properties to the product. In both cases it is crucially important, that the additional components of rubber compound and the product are well bonded to the elastomer segments of the matrix.

In this module of the Virtual Education for Rubber Technology (VERT) we tend to provide a general background and awareness of reinforcing fibres, and to give the rubber technologists an improved basic understanding of the uses, processes and potential problems associated with the use of fibre components in rubber products. The VERT module “The raw materials and compounds” handles the fundamentals of the topics of reinforcing additives and fillers.

PART I

The first part of this module covers the history, definitions, classification and basic technology of the processes used in preparing textile fibres. In the context of the properties of reinforcing fibres, particular attention is given to the aspects of adhesion, adhesive treatments and processing and the assessment of adhesion.

History and background of rubber reinforcement

The earliest rubber products utilizing reinforcements were flat cotton composites like waterproof garments. The next development steps were the development of hoses, and later on, pneumatic tyres. The first tyres were based on a tube strapped to the wheel by means of rubberized fabric. Later, the inner tube with a separate outer tyre
was evolved. The outer tyre was made from layers of square woven cotton canvas and rubber, with wire beads to hold it in place on the rim. In the first decennia of nineteenth century, the canvas was replaced by cord fabrics, and during the same time carbon black was starting to be used in tyres, leading to doubled life of the tyres (mileage at that time being about 6000 km).

To further improve tyre performance, new artificial fibre, rayon, for the reinforcing plies of fabric was to be employed. When using cotton, there had been no problem in adhering the rubber to the textile inserts. The search to find a system to improve the adhesion led to the development of adhesive dips. These were originally based on natural latex and casein, but soon the casein system was replaced with a resorcinol/formaldehyde resin and later, especially when rayon and polyamide were introduced, ter-polymer lattices, containing e.g. vinyl pyridine as the third monomer, were developed to give improved adhesion.

With the introduction of polyester the standard RFL systems did not work. The first systems found to give good adhesion to polyester were based on very active isocyanates from solvent solution, and later, aqueous based process was achieved. In the 1970’s, the use of newly introduced aramid fibres necessitated the development of new adhesive systems.

In 1980’s and later the development of e.g. polyethylene naphtalate (PEN), polyvinyl alcohol (PVA), as well as liquid crystal polymer (LCP) fibres, glass, carbon and steel wire fibres has offered new opportunities to high performance rubber product development.

With each new reinforcing agent, either synthetic polymer or metal wire/cord type introduced, special adhesive systems had to be developed, in order to obtain the optimum performance from the rubber composite products. Today, composites are available which satisfy even the most stringent performance requirements met under the widely varying application fields of elastomer-based products.

Production and properties of textile yarns

There are at present five main types of organic fibres used in reinforcements for rubbers. Cotton is still in use in many applications, but is more and more replaced by synthetic fibres. It is worth mentioning that in Europe, the term synthetic is used only when referring to fibres in which the fibre-forming polymer is not of natural origin. Thus in Europe, e.g. rayon, which is based on naturally occurring cellulose, is classified as man-made or artificial but is not considered to be a synthetic yarn. Rayon, the first of the successful artificial fibres, is chemically very similar to cotton, but the various processes introduce certain differences in properties between the two. The first truly synthetic fibres polyamides (both PA 6.6 and PA 6) offer certain advantages over the cellulosic fibres. On the other hand, polyester has the strength similar to nylon, but has a higher modulus. The aramids,
with considerably higher strength and modulus, are the latest reinforcing yarns. They have relatively high cost, but e.g. their strength/cost ratio, comparable with steel wire has made their applications steadily increasing. A relatively new fibre family in rubber reinforcing field, PEN, is emerging to the market in the applications where good heavy duty properties are required.

_The material presents the production methods and the general properties of the following fibers: cotton, rayon, special rayons, like Lyocell, polyamides, especially nylon 6 and nylon 6.6, polyester, high performance polyester fiber called polyethylene naphtalate (PEN) and aramid._

Yarn and cord processing

As a rule, it is a necessity to modify the yarn in order to obtain the optimum benefit from their incorporation as reinforcement in elastomeric composites.

Depending on the product to be reinforced, either single-end yarns or cords (several twisted yarns twisted together) are the preferred form, or in some cases (particularly in tyres) cord-fabric form, where the cords have been assembled together into a woven cord-fabric. For most other applications, woven fabrics constructions are applied, and it is generally necessary to modify the yarn, rather than using them in as-produced form.

The material presents the yarn preparation process. The most common methods of obtaining the required structure of yarn are twisting and texturing. The purpose of twisting is to prevent filament breakage, to improve fatigue resistance and to improve weaving workability. In the texturing procedure the continuous filaments of the yarns are tangled and looped together, giving a bulky and coherent yarn.

For many industrial reinforcement applications, it is desirable to assemble the yarns together into a coherent form using various weaving or knitting techniques and designs. The majority of rubber reinforcements are based on weaved fabrics, although e.g. knitting or non-woven systems can offer certain advantages for special applications.

The main operating principle of – even modern weaving machines – is to achieve the interlacing of two sets of yarns (warp and weft) at right angles to one another, to produce a fabric.

In selecting a fabric for a specific application some aspects has to be taken into consideration: the physical properties of the woven fabrics, the fiber type and fabric construction.
Rubber/textile composite assembly (fabrication)

It is important to avert any contamination of the surfaces of the rubber compound or the textile on assembly of the composite. Contamination can seriously reduce the obtained adhesion. Direct calendering or spread coating is the best method to use, to ensure intimate and clean contact between the rubber and the textile surface.

All the precautions are required to avoid the migration to the surface, or blooming, of any of the ingredients, or any other surface deposits interfering with adhesion.

It is also important to avert any entrapment of air or volatile materials during the assembly. A spiked roller is often used to allow egress of air or profiled compaction roller, with a slight bow in the center, is used to push air to the outside of the composite which is assembled.

The most common volatile material is moisture. To eliminate any moisture absorbed by the textile materials containing cotton or rayon, must be dried before rubberising or assembly. The regain of nylon and polyester is normally sufficiently low for the moisture to cause any problem. If nylon has been held under high temperature and very high humidity, a drying stage may be required before using the material.

It is important that all solvent, if solvents are used, is allowed to evaporate off before assembling the composite. Any surface treatment which are applied during prior processes to avoid the sticking together of sheeted rubbers, must be removed.

Coating and calendering are the two most important processes used to combine textiles and rubber.

There are several parameters to be controlled during calendering. The behavior of the applied compound is the most important. The scorch and plasticity of the compound should be suitable for processing. Calender bowl temperature must be controlled to give homogeneous coverage and surface smoothness. The tension of the fabric in the calender nip must be right. Thickness of the rubber applied is probably the most critical parameter.

Solvent coating or spreading is one method of combining the textile and the rubber. This is normally used for thin rubber coatings or applying an adhesive layer, other than RFL system. Knife coating, using a dough, and lick roller coating are two basic systems of coating fabrics.

Heat-setting and adhesive treatments

Before the fibres can be used for elastomer reinforcement some treatments are often needed. If using cotton only drying to reduce moisture as pre-treatment is needed. If using rayon...
additional treatment is needed drying as well as drying. Shrinkage causes some problems while using synthetics fibres. Moisture is not normally a problem with these, but special adhesive treatments are still needed. Last stage in textile manufacturing is combined heat-setting and adhesive treatment. Nowadays there are sophisticated machines for single-end cords and for fabrics as well. Those machines adjust all the needed adhesive and physical properties for textile very accurately.

Synthetic yarns like nylon and polyester have a high shrinkage. Some changes in physical properties happen also if the yarns are exposed high temperature, especially in modulus and elongation. Textile is treated at elevated temperatures under tension during manufacturing, this process is known as heat setting. During the heat-setting process crystallinity of synthetic yarns is modified bringing the desired changes in properties. The general physical properties of the cord or fabric can be adjusted by selecting the conditions of heat setting. Heat setting stabilises the yarn and reduces the changes in properties on exposure of the yarn to heat.

Adhesive treatment is usually combined with the heat-setting process. The fibre type dictates the actual adhesive system used. Some modifications to the basic systems are often necessary to obtain optimum adhesion to the special elastomers.

Textile components made from cotton do not usually need any adhesive treatment. Adhesion is obtained by the mechanical anchoring of the staple fibre ends into the elastomer matrix. Rayon requires an adhesive pre-treatment in order to achieve bond strength for reinforcement of elastomers. The original systems were based on casein/natural latex mixtures, but the casein component is nowadays replaced with resorcinol/formaldehyde resins giving improved adhesion and more reproducible results. The 6.6 and 6 nylons require a similar RFL system as rayon. With polyesters the basic RFL systems do not give satisfactory adhesion and alternative systems or pretreatments have been developed. The original systems, based on solvent application of isocyanates, did not require further treatment. Those solvents are not favoured in production environments because there are both health and fire risks. Instead of using solvent solutions of the straight isocyanate, used dispersions of blocked isocyanates. These were used as a pre-dip, followed by an RFL dip giving reasonable adhesion. Later the blocked isocyanate dispersion was added to the RFL in a single bath system giving results slightly inferior to the two bath systems. Further development led to the system, in which a water miscible epoxy is added to the blocked isocyanate dispersion. Then the polyester is given a second dip with a standard RFL system. This system gives good levels of adhesion and is quite widely used. Aramid is chemically related to the nylons, but do not give as good adhesion when treated with the RFL dips. The two-stage systems can be used, but under certain conditions these may have deleterious effects on the dynamic performance of the treated cords. Simple pretreatment for first dip of an epoxy is used, based on the reaction of epichlorohydrin with glycerol. The first dip is followed by a standard RFL second stage.
Textile cord testing

This part of the material presents the different methods used in textile cord testing. The main parameters tested are: twist of a single yarn and folded yarn, thickness of the cord, linear density of a single yard and folded or cabled yarn, amount on dip of dipped cord, tensile properties (breaking force and elongation), shrinkage (boiling water and hot air), drawing properties (draw tension at given draw ratio, drawing temperature and drawing speed), stiffness, adhesion (H-test), strip adhesion (single textile cord and rubberised textile cord).

PART II

In the second part, the basic technology of steel based fibres and the processes used in preparing these components are handled. Again, attention is directed to the aspects of adhesion, to illustrate how the optimum reinforcement and performance for a particular application is achieved.

Steel cord

Steel is a metal alloy whose major component is iron, with carbon content between 0.02% and 1.7% by weight. Carbon is the most cost effective alloying material for iron, but many other alloying elements are also used. Currently there are several classes of steels in which carbon is replaced with other alloying materials, and carbon, if present, is undesired. A more recent definition is that steels are iron-based alloys that can be plastically formed (pounded, rolled, etc.).

Steel cord is a major component used for reinforcing a radial tire. Steel cord is stronger than fibre materials, have excellent heat and fatigue resistance with no contraction. Steel cord is a tire reinforcement material with the highest growth rate.

Steel cord has four basic components: filament or wire, strand, cord and spiral warp. The construction of a tyre cord is normally defined by structure, length and direction of lay and by product type. The material presents some general characteristics and the manufacturing process of steel cords.

Bead wire

A bead wire is a major component used for reinforcing radial tires, while protecting the carcass plies from rubbing against the rim. Beads are bands of high tensile strength steel wire encased in a rubber compound. Bead wire is coated with special alloys of bronze.
(copper and tin) or brass (copper and zinc). Coatings protect the steel from corrosion and improve adhesion.

The general characteristics of bead wire is presented in the material along with the manufacturing process and packing and storing of bead wire coils.

Steel belt processing

To produce steel belts, the steel cords must go through a calendering process or a steel belt extruding process, e.g. steelastic process. Steel belts give the tire strength and dent resistance, while remaining flexible. Passenger tires are usually made with two belts. The individual cord plies of a cross-ply tyre are arranged in a criss-cross pattern at a certain angle – known as the cord angle. This angle determines the tyre’s characteristics. The material presents the calandering and extruding processes and machinery in detail.

Steel wire and cord testing

Steel wire and cord testing part of the material presents the parameters measured from steel cords: residual torsion of the cord, straightness of the cord (arc height method), length and direction of lay, linear density, tensile properties (breaking force and elongation), cord thickness, static adhesion to rubber compound, flare and mass and composition of brass and coating. The testing of rubberized steel cords include determination of rubberized ends, thickness and square meter weight. Testing of bead wire includes the determination of tensile properties (breaking force and elongation), bead wire thickness, static adhesion to rubber compound and bead wire coating.

PART III

The third part of this module sheds light to the principles of applying fibre reinforcement techniques in different rubber products. Short descriptions are presented on the use of reinforcing fibres and components in the tyre products as well as in industrial and consumer rubber good applications.

Product reinforcing

Above described reinforcing materials are used in different kinds of products. The main groups are tyres, industrial rubber products, belting applications and hoses. The term “industrial rubber products” represents a very broad product array ranging from single-component all-rubber articles such as roofing or other membranes through to more sophisticated composites such as timing belts and multilayer high-pressure hoses. Belting
applications include conveyor belts, power transmission belts, V-belts, timing belts, flat belting and cut-length belting.

A hose is actually a reinforced tube. The reinforcement of textile yarn or steel wire is applied by spiralling, knitting, braiding or circular loom weaving. There is a wide range of hose types available, depending on the type of medium to be carried, the pressure and the volume to be transported. Special hose types include fuel hoses, coolant hoses and oil suction and discharge hoses.

Miscellaneous applications of reinforced rubber

The material has covered the major areas of reinforcement of rubbers, i.e. tyres, different belts and hoses, but there are still numerous applications, which do not fall within these groups. For instance, there are applications of coated fabrics for various purposes, different diaphragms, and snowmobile tracks, just to mention a few.

The major applications of coated fabrics are in inflatable constructions and coated rubber sheeting, used in the flat state. There are many uses for such constructions, not only for inflatables but also for many shielding applications, oil booms, dams and flexible storage systems etc.

Inflatable reinforced structures are typically manufactured from fabric, which has been treated with a relatively thin coating of the matrix polymer. For some applications, a thicker coating is required and is usually applied by calendering. After preparing of the required thickness of rubber, the unvulcanized sheets are usually rolled onto a steel tube with a light untreated separating nylon fabric, to prevent the layers sticking together, and then cured in an autoclave. Examples of inflatable applications include inflatable boats, oil booms, inflatable dams and buildings.

Besides the applications based on inflated structures, there are many applications where similar materials are used flat or filled with some material, for storage or transport. There are, of course, many applications just for flat-coated sheeting.

In different liner applications, the coated fabric is used to contain a liquid in the reservoir, or to form an impermeable layer on the bottom or walls or it may be used on the surface as an evaporation hindrance, etc. Other examples of applications of non-inflated structures are flexible storage tanks, hovercraft skirts and snowmobile tracks.
Tyre dynamics, tyre as a car component
Virtual Education in Rubber Technology (VERT), FI-04-B-F-PP-160531

SUMMARY

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The module ‘Tyre dynamics, tyre as a car component’ deals with the tyre properties in relationship with car performance. The combination of tyre and vehicle is expected to perform in a satisfactory way by the person who buys and drives the car. This includes a good handling comfort, a safe performance in terms of cornering and braking, and good steerability. There is an objective side to this in the sense that the car behaves well under controlled driver input. But there is also a subjective element. The vehicle should ‘feel good’. In addition to these handling and comfort aspects, tyres are nowadays also judged with respect to environmental impact, e.g. rolling resistance and noise. And finally, the tyres should last long, i.e. wear should be limited.

All of these aspects are discussed in this module, which consists therefore of the following five parts:

1. Tyre handling performance
2. Driver judgement of tyre handling characteristics
3. Rolling resistance
4. Tyre noise
5. Tyre wear

The first sub-module on tyre handling performance discusses the tyre-road interface and defines relevant road surface parameters, tyre input and output parameters (contactforces, moments, slip, rotations), the effective tyre rolling radius. Distinction is made and interpretations are given for radial-ply and bias-ply tyre designs. Next, the rolling tyre is discussed, with emphasis on the physical phenomena in the contact region. The same is done for the tyre under braking or driving conditions, with the rolling tyre as a reference. This means the definition of theoretical and practical longitudinal slip, and the indication of adhesion and sliding parts in the contact area, in relationship to brake- or driveslip, speed and tyre load. The braking wheel is treated in a dynamic sense, and the related (tyre-based) models are linked to longitudinal vehicle models. The full nonlinear longitudinal tyre characteristics are discussed, including empirical tyre models (Pacejka Magic Formula model). This also includes the effect of different surface textures, wet road conditions, tyre wear and tyre speed. A similar treatment is given on the tyre under cornering conditions, with definition of lateral slip, relationship with vehicle cornering performance, effect of road texture and speed, full nonlinear tyre characteristics and
empirical (Pacejka) tyre models. For cornering conditions, pneumatic trail and aligning torque are important and treated in some detail, as well as the impact of changing tyre load and camber on tyre contact forces.

Next, it is assumed that longitudinal slip and lateral slip may occur simultaneously, resulting in a discussion on combined tyre slip (combined braking and cornering). In addition to an empirical tyre description, some physical models are treated related to the brush approach, the description of the tyre as an infinite stressed string and the combined brush-string model. It is shown how the essential qualitative tyre characteristics can be described as a result of fundamental assumptions on the physical performance of tyre belt and contact compound, both in structural sense and with reference to the behaviour in the contact area.

The final part of this submodule treats the transient (first order relaxation) behaviour and the dynamic tyre behaviour (including belt dynamics). Transient behaviour is relevant for fast variations of tyre slip. Dynamic behaviour needs to be taken into account in combination with smart chassis control measures, possibly in combination with irregular road surfaces (ride durability), driveline vibrations, complex shimmy, etc. The approach as treated is based on the rigid ring assumption (also known as SWIFT model: Short Wave Intermediate Frequency Tyre model), and depends on a preprocessing of the road surface profile accounting for the tyre enveloping properties. This submodule closes with some remarks on the experimental assessment of tyre characteristics.

The second submodule on **driver judgement of tyre handling characteristics** gives a survey of the impact of different tyre and road surface parameters on the judgement of vehicle handling performance. Judgement distinguishes between objective vehicle performance assessment, with well defined steering and braking inputs, and subjective performance assessment where the driver may be allowed to respond to vehicle behaviour. Such subjective assessment may be carried out through a specific task as determining a maximum speed (lane change), minimum lateral deviations, steering motions (straight lane test), etc. It may be based on rating scales and it may be based on open questions. Objective assessment is usually linked to ISO-based reference tests. The parameters being discussed cover tyre construction parameters (compound, ply-type, belt and carcass material), tyre dimensions, service parameters (tyre pressure, speed, wet-dry conditions, temperature), performance measures (i.e. cornering stiffness) and ageing parameters. Subjective and objective assessment strategies are discussed in some detail including the relevant performance metrics.

The third submodule on **tyre rolling resistance** starts with the definition of rolling resistance and a discussion how rolling resistance can be explained physically. What is the impact of material properties, loading, road conditions, and how do the various tyre parts contribute to rolling resistance. In the next sections of this submodule, the different possible sources for varying rolling resistance are treated. This includes braking and driving torque, slip angle and camber angle, the effect of changing temperature (e.g. start-up conditions), varying inflation pressure and tyre load, forward velocity and wear.
This submodule also discusses rolling resistance on a wet road, on a drum (vs. a flat road).

The fourth submodule on **tyre noise** discusses the relative impact of the tyre on the emitted vehicle noise in comparison to powertrain and aerodynamic noise. For the tyre, it treats the various sound generation mechanisms such as tread impact, air pumping, slip stick and stock-snap. Next, it treats the sound enhancement mechanisms such as the horn effect, the organ-pipe effects (in channels formed in the tyre foot-print) and Helmholtz resonator mechanism (air resonant radiation), carcass vibration and internal acoustic resonance. Some tyre noise spectra are shown as illustration.

Factors that contribute to tyre noise (and which may be manipulated to reduce tyre noise) include external factors such as pavement, speed, load and braking/driving input. They also include internal factors such as tread, wear, structure, material, size and pressure.
The submodule closes with some remarks on modeling of tyre noise.

The final submodule on **tyre wear** starts with a discussion on wear mechanisms such as adhesive wear, abrasive wear, erosive wear, ageing, fatigue and excessive wear (e.g. flat spots, cupping, high temperature wear, ...). Tyre and vehicle parameters and characteristics have an impact on tyre wear, and wear has an impact on tyre and vehicle performance. Typical relevant tyre based parameters and characteristics include structure and ply-type, material (rubber hardness, silica, ...), tyre pressure and tread pattern.

In order to drive a car, engine power, braking power and cornering forces have to be transferred from car to road through the tyres. More power means more wear, where certain chassis control systems (ABS, ESP, active suspension, ...) may change this relationship. Very important is the wheel alignment (camber, toe angle).

The impact of tyre wear on vehicle performance is mainly related to the reduced tread depth, which significantly changes the slip characteristics on a dry or wet road. It may also lead to changed filtering properties for road undulations, and a different fuel consumption (rolling resistance).

Wear strongly depends on the driving conditions, influenced by the driver, road surface properties and weather. Wear mechanisms can be observed experimentally, outdoor on the road, indoor on a drum and on dedicated material testers.

There exist different wear indicating strategies.

The module includes queries for on-line verification that one is sufficiently mastering the material. The questions are, to a large extent, asking for understanding the mechanisms, rather then asking for facts. In that way, the student is forced to process the material as offered in the module to a sufficient abstract level, supported by continuous feed-back.