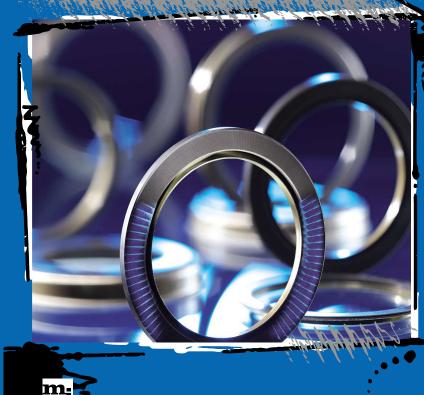
**VERLAG MODERNE INDUSTRIE** 

# Technical Elastomers

The basis of high-tech sealing and vibration control technology solutions



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Freudenberg Sealing Technologies

### verlag moderne industrie

# **Technical Elastomers**

The basis of high-tech sealing and vibration control technology solutions

Meike Rinnbauer



This book was produced with the technical collaboration of Freudenberg Sealing Technologies GmbH & Co. KG.

Translation: Flanagan Language Services, Aingeal Flanagan, Köln

© 2007 All rights reserved with sv corporate media GmbH, D-80992 Munich, Germany www.sv-corporate-media.de

First published in Germany in the series Die Bibliothek der Technik
Original title: Technische Elastomerwerkstoffe
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Illustrations: Freudenberg Sealing Technologies GmbH & Co. KG, Weinheim Typesetting: abavo GmbH, D-86807 Buchloe Printing and binding: Sellier Druck GmbH, D-85354 Freising

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# **Elastomer development**

# From natural rubber to high-tech material

Age-old material

Discovery of vulcanization

High-tech products

Additional functions

Humankind has been familiar with elastomer materials in the form of natural rubbers for centuries. Natives in Central and South America used this material for seals and balls. The term "caoutchouc" comes from the Mayan language (cao = tree and ochu = tear) and is a collective term for all non-cross-linked elastic polymers. The accidental discovery of vulcanization (curing) by Charles Goodyear in 1839 paved the way for the manufacture of highly flexible cross-linked materials (elastomers), which in turn made it possible to use these materials for countless technical applications. Today, elastomers are indispensable for seals and vibration-control applications. Were it not for elastomers, there would be no such thing as cars or planes, and hydraulics and pneumatics would be unimaginable. Many of today's elastomer components are high-tech products that meet even the most exacting requirements regarding temperature, chemical resistance, and wear. A radial shaft seal (Simmerring®) is a perfect example of a highly developed elastomeric component. It works like a microscopic pump that transports lubricants or gases under the sealing edge and back into the oil chamber, thereby ensuring adequate lubrication between the shaft and the seal (Fig. 1). In addition to performing a simple sealing function, seals can also assume other functions when combined with modern sensor technol-

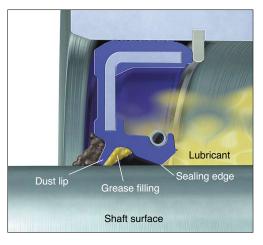


Fig. 1:
The operating principle of a Simmerring® (cross-section) featuring an additional dust lip to protect the seal against dirt and dust

ogy. The increasing multi-functionality of modern elastomeric components means that expertise and a wealth of experience are needed for targeted elastomeric development.

#### **Basic principles**

Polymers are very large molecules that are formed by the linkage of a large number of very small structural units (monomers). The monomers are linked by means of functional, reactive groups, thereby creating composites that exhibit completely different properties to the starting materials. The molecular structure of polymers can be linear, branched, or crosslinked. Depending on the orientation of the molecule chains, a differentiation is made between polymers in an amorphous and a partially crystalline state. The degree of polymerization – i.e. the number of monomers in a polymer chain – has a significant influence on the mechanical properties of the polymers. As the crystallinity or density of the polymer

Degree of polymerization

#### Viscoelastic behavior

#### Glass transition temperature

increases, so too do the melting range, tensile strength, stiffness (elastic modulus), hardness, resistance to solvents, and impermeability to gases and vapors.

Polymers of high molecular weight such as elastomers demonstrate a pronounced viscoelastic behavior compared to most other materials when subjected to mechanical loads. Depending on the load exerted, the deformation that occurs is of an elastic or a viscous nature. The key to understanding the mechanical properties at various temperatures is a knowledge of the processes that take place in the transition zone between the defined states, which is, among other things, characterized by the socalled "glass transition temperature" or Tg. The glass transition is a characteristic variable for every polymer. Below the glass transition temperature, the proper motion of the molecules – which is also known as Brownian motion freezes. The material is in a hard, glassy state. When the glass transition is exceeded, the molecules become mobile once again and the polymer changes over to a soft, rubbery-elastic state (Fig. 2). If the temperature continues to rise, viscous flow occurs followed by decomposition of the polymer.

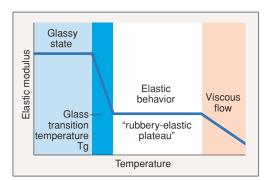
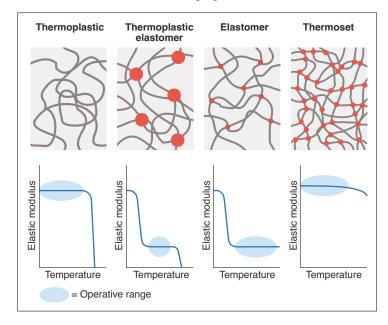


Fig. 2: The relationship between the elastic modulus of polymer and temperature

Polymer materials are categorized according to their structure, their mechanical deformation behavior and, correspondingly, their properties and areas of application (Fig. 3). Thermoplastics are made up of long and linear or loosely branched polymers that are not cross-linked. At room temperature they are in a state that is somewhere between glassy and ductile. Thermoplastics can have amorphous or partially crystalline structures. In amorphous thermoplastics, the polymer chains are arranged in a random manner both in the molten and in the solid state. Partially crystalline thermoplastics are amorphous in the molten state. However, when solid, there are areas in which the polymer chains are arranged parallel to one another. The degree of crystallinity has a significant influence on the mechanical properties of

#### **Thermoplastics**

Fig. 3: Schematic structure of polymers and elastic modulustemperature curves



#### **Elastomers**

the material. Temperature increases and heavy shearing plasticize thermoplastics, at which point they can be formed or molded.

Elastomers are created by the loose crosslinking of amorphous, often highly branched polymers (e.g. natural rubber). This loose fixation of polymer chains by chemical bonds results in the highly elastic behavior above the glass transition temperature Tg that is so typical of this polymer material (the so-called "rubbery-elastic plateau").

Unlike thermoplastics, the molding of elastomers is associated with a chemical reaction (cross-linking). In the case of higher degrees of cross-linking, the Tg is pushed upwards until almost all molecular movements are prevented by the rigid fixation of the polymer chains (as is the case, for example, with ebonite). This means that only minimal displacements are possible when subjected to external loads. Close (three-dimensional) cross-linking or "hardening" leads to *thermosets*, which, like elastomers, are irreversibly destroyed once the decomposition temperature is exceeded. Examples of thermosets include epoxide resins or phenol formaldehydes.

Thermoplastic elastomers (TPE) constitute a hybrid class. Between Tg and the melting point and/or the softening point, they behave like elastomers. They are, however, thermoformable at higher temperatures (i.e. >100°C). In many TPEs, a thermoreversible structure with elastic properties is formed during the cooling phase as a result of physical crosslinking across (partially) crystalline areas. This means that – as is the case with thermoplastics – exceeding the softening point to even the smallest degree can cause irreversible loss of component geometry in the application.

# **Elastomers and their properties**

The ASTM standard D 1566 (ASTM: American Society for Testing and Materials) defines elastomers as high-polymeric, organic networks that are capable of absorbing large deformations in a reversible manner. This property, coupled with the fact that elastomers are capable of absorbing mechanical energy, means that elastomers can be used to manufacture products that accommodate tolerances, allow for movement between different components, make it possible to create static and mobile seals, diminish and damp vibrations, and assume spring functions.

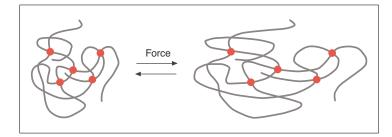
High-polymeric organic networks

# The viscoelastic behavior of elastomers

Unlike energy-elastic solids such as metals or alloys, elastomers are entropy-elastic. The force behind this elasticity is entropy, i.e. the degree of disorder which is greater in the entangled, disordered state of the polymer chains than in an arranged, extended, orderly state. In entropy-elasticity, the distance between the atoms does not alter; the individual

**Entropy- elasticity** 

Fig. 4: Entropy-elasticity model



#### **Thermosets**

**TPE** 

#### **Entropy** decrease ...

#### ... and increase

Fig. 5: Spring-damper model used to illustrate elasticity

chain segments are merely pushed towards one another. If stress is applied to the elastomer in this state, the entangled chains are transformed into an arranged and thus less plausible state (entropy decrease). When the stress is released, the original, more energyfavorable entangled state is reassumed (entropy increase). The change in entropy is the driving force behind the resilience of elastomers in the rubbery-elastic range above the glass transition temperature Tg (Fig. 4).

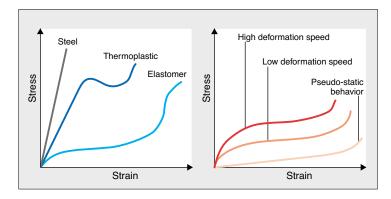
Viscoelastic behavior in elastomers means that both the elastic behavior of solids (reversible) and the viscous behavior of fluids (irreversible) can be observed. Depending on the load applied, one or other of the properties is more pronounced (Fig. 5). At low temperatures and high deformation speeds, the solid material behavior dominates, while viscous behavior can be observed at high temperatures and low deformation speeds. The latter leads

State	Cause	Working m	odel
Energy elasticity	Based on reversible changes in the vibration and rotation conditions of atoms.	Spring	
Entropy elasticity	Based on the largely reversible displacement of molecule segments while retaining the center of gravity of the molecule (micro-Brownian motion).	Spring	Damper
Viscous flow	Based on the irreversible dis- placement of entire molecules towards one another (macro-Brownian motion)		

to creep, stress relaxation, or cold flow. Viscous flow can be suppressed to a great degree by fixing the chains to one another (crosslinking). In other words, loose cross-linking ultimately causes typical rubbery-elastic (elastomeric) behavior. The viscoelasticity of elastomers results in a pronounced time- and temperature-dependency for a large number of physical and in particular mechanical properties. In the case of steel, for example, there is a linear relationship between stress and strain, whereas with elastomer, there is a non-linear relationship between the two. This non-linear relationship is demonstrated among other things by the elastomer's dependency on the deformation speed (Fig. 6).

The consequence of this dependency is that elastomers react with great sensitivity to changes in test conditions. This is why problems are frequently encountered in practical operation when correlating simple physical test results with the actual prevailing loads exerted on an elastomer component in the installation space (the complex of loads acting on the component). This means that it is absolutely essential for exact specifications to be

Fig. 6: Stress-strain diagram Left-hand diagram: a comparison of steel, thermoplastic, and elastomer Right-hand diagram: the behavior of elastomers at different deformation speeds



prepared for an elastomer component in order to ensure that the most important properties of the product can be reproduced in tests.

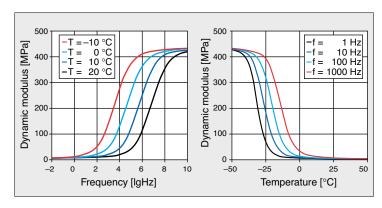
#### The correlation between frequency and temperature

In practice, a leap in the mechanical properties of elastomer are noticeable both at low temperatures and at high frequencies. This leap is caused by the viscoelastic behavior of elastomers. If a load generated by pressure or tensile force is exerted on the elastomer for varying periods of time, there is a correlation between the frequency of the load and the thermal behavior. Because of the viscous proportion in elastomer, the stress that occurs during deformation is partially reduced by chain displacements (micro-Brownian motion). The time required for this is known as relaxation. As the temperature decreases, the chain movements in the polymer slowly stop and the length of time needed to decrease stress increases. The elastomer hardens and becomes glassy. If the load frequency increases, the chain mobility no longer suffices for absorption of the deformation. The material appears to be "frozen". This effect is known as dynamic hardening. This means that an increase in frequency has the exact same effect as a drop in temperature (Fig. 7).

**Dvnamic** hardening

Relaxation

Time-temperature correspondence principle Accordingly, the glass transition temperature Tg depends not only on the method of determination, but also on the test frequency, and increases by approximately 7 Kelvin per frequency decade. This effect is known as the time-temperature correspondence principle. The result of this principle is that an increase in frequency at low temperatures leads to a



premature hardening of the material (increase in the dynamic modulus).

This influence of relaxation, which depends on temperature and frequency, must therefore be taken into account when designing components, especially dynamic seals.

Fig. 7: The time-temperature correspondence principle: dependency of the dynamic modulus on frequency (left) and on temperature (right)

#### The systematization of elastomers

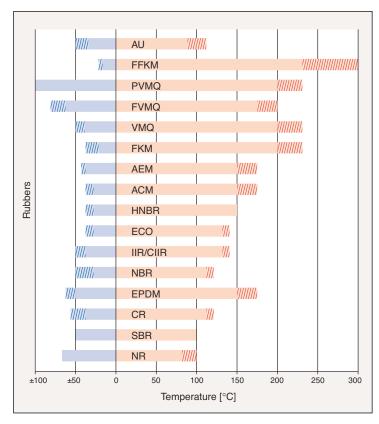
ASTM D 1418 defines a systematization for elastomers and a set of abbreviations. The ab-

Table 1: The systematization of elastomer types

Last letter in the abbreviation	Meaning	Example
М	Rubbers with saturated chains of carbon atoms, no double bonds	EPDM, ACM, EVM, FKM, FFKM
R	Rubbers with double bonds in the carbon chain (unsaturated)	NR, CR, SR, SBR, IIR, NBR, HNBR
0	Rubbers with oxygen in the polymer chain	CO, ECO
Q	Rubbers with silicon and oxygen in the polymer chain	VMQ, FVMQ
Т	Rubbers with sulfur in the polymer chain	Polysulfide elastomer
U	Rubbers with carbon, oxygen, and nitrogen in the polymer chain	AU, EU

Fig. 8: Usable temperature range for elastomers: the shaded areas indicate the usable temperature ranges to which standard types can be exposed for brief periods only or which are covered by special types

breviations are made up of a combination of between two and four letters (Table 1). The first letters describe the base polymer, the last letter indicates the chemical structure of the elastomers. For example, all elastomers with main chains containing only carbon atoms and no double bonds (reactive areas) are referred to as M-types. If the main chain contains double bonds, these elastomers are referred to as *R-type* elastomers. These are also referred to as unsaturated or diene rubbers.



Polysiloxanes differ from organic rubbers in that the main chain is not made of carbon bonds, but alternating silicon and oxygen atoms. These elastomers are known as Qtypes. These compounds are also known as silicone rubbers.

Figure 8 provides an overview of the thermal application ranges for the various types of elastomers (for properties and areas of application, please refer to the appendix on pages 68 and 69).

Silicone rubber

Knowledge of

the range of

application

### **Factors that influence** material behavior

Elastomers are sensitive to light, ozone, high temperatures, a large number of fluids and chemicals, and wear. This means that not only the usable temperature range, but frequently also the elastomer's chemical resistance and swelling behavior is of major significance when selecting a suitable sealing material. It also explains why information about the range of application – e.g. the fluid or gaseous media with which the material will come in contact – plays a decisive role in determining the functional capability of an elastomeric material. However, when developing the elastomeric compound, not only must the chemical and physical factors of environmental influences be taken into account, but also the processes of interaction that are created by the polymer and the compound ingredients and which determine the overall physical properties of the elastomer. Together, all of these factors have a significant influence on the life of the final component.

**Compound ingredients** 

Elastomers are multi-component systems in which each component has a very specific role to play. When developing the compound, four main effects must be achieved: the reinforcement of the elastomer by fillers, the improvement of processability, the cross-linking of rubber using curing agents, and the protection of the elastomeric component against damaging external influences.

The basic properties of an elastomeric compound are determined by the polymer and are decisive for the performance of the seal. For example, although it is the polymer that determines the elastomer's low-temperature properties, plasticizers can improve these properties within certain limits. However, when adding plasticizers, it is important to take into consideration that they can be extracted from the elastomer through contact with lubricating oils and can evaporate at high temperatures. This is why it is important at the development stage to take account of the operating conditions (e.g. temperatures) to which a seal will be exposed.

So-called reinforcing fillers such as carbon blacks or silicas also have a significant influence on the material properties of the elastomer. By varying the type and amount of fillers used, the physical properties of the elastomer can be adapted to suit the intended application. The specific surface, the structure, and the surface activity of the fillers largely determine the reinforcement effect. The principle is based on the interaction of the filler with the polymer matrix or - if the filler content is sufficiently high - on the formation of filler networks that are superimposed on the chemical polymer network. Reinforcing fillers – in other words active fillers - have a particle diameter of between 10 and 100 nm (nano particles); inactive fillers, on the other hand, have a particle diameter of between 500 and 1,000 nm. Carbon blacks are classified using an ASTM code that characterizes the activity of the carbon blacks. The smaller the number, the greater the reinforcing effect of the carbon black. Because active carbon blacks have a much greater influence **Plasticizers** 

Reinforcing fillers

Active carbon blacks

Four main effects

#### Homogeneous dispersion

on the properties of elastomers than inactive fillers, a dependency of mechanical properties such as tensile strength, abrasion resistance, or tear strength on the structure and surface of the carbon blacks and the filler content can be observed (Fig. 9). A homogeneous dispersion (distribution) of fillers in the polymer matrix is the prerequisite for a high-

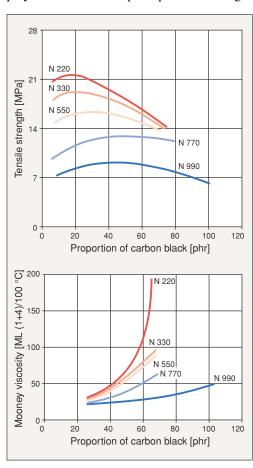


Fig. 9: The effect of active (N 220, N 330). semi-active (N 550). and inactive carbon blacks (N 770, N 990) on compound properties such as tensile strength and viscosity is largely determined by the type and proportion of the selected carbon black (phr = parts perhundred rubber).

quality elastomeric product. This is why carbon blacks that ensure good dispersibility and high processing reliability are now used in the production of engineering elastomeric materials.

White fillers such as silicas exhibit similar reinforcement potential to carbon blacks. However, silicas have a marked tendency to agglomerate. They create strong filler networks that are responsible for the reinforcement effect in the polymer matrix. This is why compounds with active silicas are much more difficult to process than compounds with the same amount of carbon black fillers. Moreover, because of their polarity, silicas disrupt the cross-linking with sulfur accelerator systems, which in turn slows down the crosslinking process. Consequently, when replacing carbon blacks with silicas, the cross-linking chemistry must be adapted accordingly.

#### The influence of the cross-link density

Curing or cross-linking is the name given to the production stage during which an elastomeric component is molded. During this procedure, chemical bonds are made that transform the rubber compound into an elastomer with tailored properties. Curing generally takes place under pressure and at increased temperatures (T >140°C) in specially constructed tools.

The cross-linking system determines the processing qualities, the chemical structure of the network, and the physical properties of the elastomers. This is why the cross-linking system chosen during the development of the elastomer compound plays a decisive role in

Silicas

**Cross-linking** as the formation stage

Sulfur and peroxide cross-linking

obtaining the desired material properties. The two most frequent types of cross-linking are: sulfur cross-linking and peroxide cross-linking. The sulfur cross-linking process consists not only of the addition of free sulfur, but also the combination of different substances that ensures the required cross-linking characteristics. In practice, this means developing a processable compound that guarantees not only reliable molding, but also economical production. The wide spectrum of available accelerators, sulfur donors, and retarding agents creates an almost endless number of possible combinations. Sulfur cross-linking is used primarily for the cross-linking of diene rubbers such as NR. SBR. BR. NBR. or CR. The importance of peroxide cross-linking has increased with the development of saturated synthetic rubber types. This type of crosslinking paved the way for the cross-linking of rubbers without double bonds in the main chain. Moreover, peroxide cross-linking can be used to improve thermal resistance. This is particularly true of NBR. However, a variety of factors such as hot-air heating, fillers containing acid groups, or peroxide decomposition products that form during the cross-linking process can prevent smooth cross-linking. The extent of the chemical bonds created between the polymer chains during curing for both types of cross-linking depends not only on the rubber type, but also primarily on the type and amount of the selected cross-linking system. This is referred to as the degree of cross-linking or the cross-link density.

The cross-link density exerts a decisive influence on material properties such as fatigue, hardness, tensile strength, permanent set, friction, and elongation at break (Fig. 10).

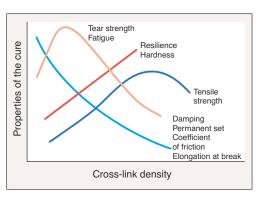


Fig. 10: The influence of cross-link density on the elastomer properties

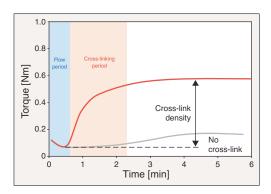
As the cross-link density increases, the elastic modulus, hardness, and elasticity increase, the elongation at break, damping, and permanent set decrease, while the tear strength and tensile strength peak before decreasing significantly again. Consequently, an optimum cannot be reached for all material properties with any one cross-link density. As a rule, the cross-link density is selected in such a way as to optimize only those physical properties that are important for a specific application.

Because it is very difficult to determine the cross-link density chemically, a mechanical variable that is almost directly proportional to the cross-link density - namely torque - is recorded at a constant temperature during the cross-linking reaction. An increase in cross-link density is indicated by an increase in torque. The machine that is used for this purpose, the so-called rheometer, comprises a temperaturecontrolled measurement chamber and a flat, cylindrical shearing disk (rotor) that moves at a constant speed. When the rubber sample is inserted, a torque is generated at the rotor shaft. This torque is registered over the course of

Cross-link density

Measuring the torque

Fig. 11: Cross-linking characteristics of elastomers determined by measurement of the torque



time and is used to estimate the cross-link density. The vulcanization curve also sheds light on the viscosity of the compound at curing temperature. One differentiates between three characteristic periods (Fig. 11):

#### Flow period

• The flow period covers the interval between the start of the measurement to the start of cross-linking, i.e. the point at which the torque starts to increase. It characterizes the period of viscous flow, which is used to fill the mold in the tool. During this period, the torque initially decreases.

#### **Cross-linking** period

• The cross-linking period provides information on the interval between the start of cross-linking to the point when the material is transformed into a dimensionally stable state.

#### **Cross-linking** completed

• The cross-link is completed when all possible cross-link points have been developed. The torque stabilizes at this point.

changes that lead to hardening, softening, or

Physical and chemical action Depending on the action involved, ageing processes in the elastomer network trigger

the loss of strength. These changes can take the form of swelling, cracking, embrittlement, or discoloration of the elastomer. An increase in temperature accelerates the ageing processes considerably. The following rule of thumb applies: for every 10°C increase in temperature, ageing accelerates by a factor of between 2 and 4. The life of the component is shortened accordingly by the same factor.

#### Damage caused by oxygen

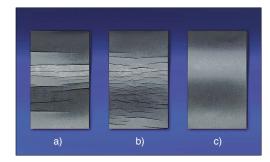
Seals are exposed to a large number of environmental influences such as oxygen, ozone, UV light, or changing climatic conditions. The combination of oxygen in the air and increased temperatures damages the elastomer matrix. This damage can either lead to an additional cross-linking of polymer chains or a degradation of cross-linking points. These in turn lead to a loss of strength, hardening, or characteristic cracking, all of which can ultimately lead to the failure of the component. Diene rubbers such as NR. SBR. and NBR which still contain double bonds in the polymer chain are more sensitive to oxygen and, most particularly, ozone, than saturated rubbers such as EPDM, ACM, ECO, etc.

In order to retard or to halt the ageing process altogether, antioxidants that have been selected to suit the elastomer type in question are added to elastomer compounds (especially diene rubbers). These antioxidants chemically neutralize the oxygen in the air so that oxidation of the polymer chains is reliably prevented. Appropriate anti-ozonants and waxes are used to prevent ozone-related damage. In the event of permanent deformation – especially in the case of increased temperatures - chemical processes (chain degraDamage to the elastomer matrix

Anti-ozonants and waxes

Elastomers age

Fig. 12: Damage to the elastomer caused by exposure to ozone: (a) with antiozonant, (b) without anti-ozonant. (c) compared with an elastomer that has not aged



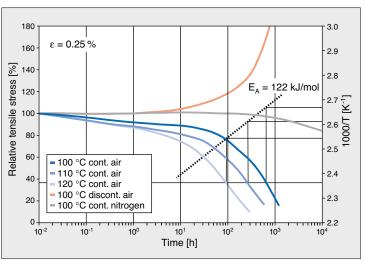
dation, reduction in the number of cross-link points, or rearrangements) that lead to a permanent change in the material can be superimposed on the physical processes. Ozonerelated damage to elastomer components is considerably accelerated if the component in question is subject to tensile stress. In this case, characteristic cracks perpendicular to the direction of stress appear. In unfavorable conditions, these cracks can lead to component failure (Fig. 12).

chemical stress

Measuring

relaxation

An exact assessment of ageing characteristics and a more detailed insight into ageing mechanisms allows chemical stress relaxation to be measured at different temperatures. In order to evaluate a variety of chemical influences better, measurements are also made by comparing them in nitrogen or in fluid media. An Arrhenius plot of the results makes it possible to extrapolate the values for long exposure times at lower temperatures (Fig. 13). In the event of thicker test specimens, the slower diffusion of oxygen in the elastomer is the limiting factor for the destruction of the elastomer matrix and the associated ageing processes. This explains why in practice, thicker elastomer components age much more slowly than thin elastomer components.



The best protection against ageing for an elastomer component depends largely on the operating conditions for which the component is intended. Only in the most favorable of cases will a single antioxidant suffice. As a rule, a combination of different antioxidants is used.

#### The influence of the medium

Whenever media such as oils and greases act upon a material, two different processes occur: physical swelling and chemical reaction. These processes can impair both the elastomer and its sealing function. The difference between the two processes is that in the latter, the influence of the media causes a chemical reaction that irreversibly changes the chemical structure of the material.

In order to find out whether an elastomeric material is suitable for use in conjunction with a specific medium, it is stored in the

Fig. 13: Estimated working life extrapolated from the measured tensile stress relaxation values (material: peroxide-cured NBR) measured at different temperatures in air and nitrogen  $\varepsilon = elongation$  $E_{\star} = activation$ energy of the ageing

process

Fig. 14: Immersion tests of elastomeric samples



Swelling and volume change

fluid of the test medium for the duration of a short-term test (Fig. 14). The medium is absorbed into the elastomer matrix by means of diffusion. In the process, the medium can accumulate on the polymer chains. What is initially a purely physical process of swelling and volume change can be overlaid by simultaneous extraction processes. In this case, elastomeric material ingredients such as plasticizers, antioxidants, or other additives migrate into the surrounding fluid medium (chemical action). As a consequence the actual changes in volume and weight observed represent the balance of fluid that has diffused into the material and the extracted constituent parts of the elastomeric material that have leached into the fluid. The swelling processes alone are completed after a few days and provide information about the suitability of the material for use in the medium in question. However, short-term tests such as this (< 3 days) cannot provide a realistic impression of the long-term changes that can be expected, because the chemical action depends to varying degrees on time and tem-

perature. This is why test runs under operating conditions are an indispensable step when evaluating a component. If the layout of the sealing environment is suitable, minor volume swelling does not pose a threat to the function of the elastomer seal. Volume shrinkage, on the other hand, can impair the sealing function in that it can result in leakage. Permeation occurs when the medium (gaseous or fluid) migrates through the material without penetrating the pores or cracks. This leads to micro leakage in the seal.

The action of the media influences many material properties such as hardness, density, tear strength, and elongation as well as electrical and optical properties such as color and surface structure. Consequently, the causes of damage are not necessarily exclusively attributable to errors in seal production, but also to external influences such as the action of oils, greases, or gases which can change the elastomer both chemically and physically. In particular, the high proportion of additives in new, fully synthetic oils can attack the sealing material chemically and destroy it. This is why seal manufacturers must have a comprehensive database of information that can be used to predict the performance and life span of the seal as accurately as possible based on interpretation of the interaction of the lubricant with the elastomer.

There is no one elastomer that meets all requirements of oil resistance, thermal resistance, and low-temperature flexibility equally. Consequently, it is essential to take into account both the surrounding medium and the temperature conditions in the intended application when selecting a suitable

Volume shrinkage impairs sealing function

Damage caused by lubricant additives

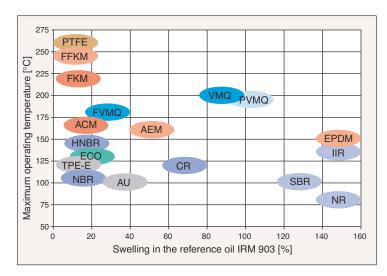


Fig. 15: The chemical resistance of elastomers in the reference oil IRM 903

#### "Like dissolves like"

sealing material. The following chemical principle applies: "Similia similibus solvuntur" (Latin: "Like dissolves like"). This means that polar elastomers (e.g. NBR) swell considerably in polar media (e.g. glycol), while nonpolar elastomers (e.g. EPDM) are not stable in nonpolar media (e.g. mineral oil) (Fig. 15). For more details about the suitability of elastomeric materials for use in selected media, please refer to the appendix in this book (see p. 70).

#### **Dynamic load**

The constant recurrence of deformation causes inner friction, which damages elastomeric materials. Over time, this leads to the internal heating of the elastomer and therefore to the formation of cracks and the destruction of the material. This process is also known as fatigue. An investigation of the material's characteristics in an attempt to predict the fa-

tigue behavior of an elastomeric sealing material is of little use because both the shape of the test specimen and the test conditions exert a significant influence. For this reason, finished parts are generally tested on test benches under conditions that are very similar to those in the intended application (Fig. 16).



Fig. 16: Test field for testing the function of radial shaft seals (Simmerrings)

External frictional load often causes material abrasion or changes the material surface. This type of wear depends not only on the elastomeric material, but also on the shaft surface, the lubrication thereof, the sliding speed, and other parameters. It is only when exact and relevant material and fatigue data from field trials are available that it is possible to use modern calculation and simulation methods to predict the component's properties and to make statements about the function over time.

Wear

Fatigue

## **Processing techniques**

Prerequisites for the production of components made of high-performance elastomer materials include the reliability of the raw material quality, exact raw material weight content, a controlled mixing process, and optimized molding processes.

#### Mixing technology

Elastomers are multi-component systems. The different raw materials with their varying weight contents and consistencies must be processed in such a way as to create a homogeneous compound. Rubber, for example, is delivered as a plastic polymer in bale or chip form and decreases in viscosity once it reaches processing temperature. Plasticizers, on the other hand, are generally delivered in oil form.

#### The mixing process

The objective of the mixing process is to distribute all necessary raw materials evenly (distributive mixing) and to break up any agglomerates (dispersive mixing) in order to achieve an optimum connection between the filler particles and the polymer. This is particularly important because the interaction of the filler particles with the polymer matrix determines several properties, among them the reinforcement of the elastomer. To illustrate the different sizes of the compound ingredients, figure 17 uses a strand of spaghetti to illustrate the length and diameter of a rubber molecule and the dimensions of its components (carbon blacks, plasticizers, and ac-

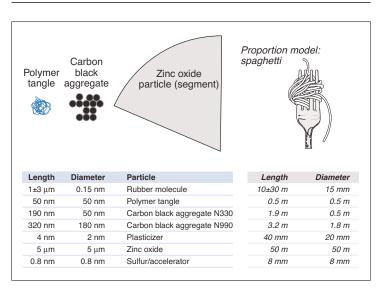
Differently sized compound ingredients

**Objective:** 

creating a

compound

homogeneous



celerators). This so-called "spaghetti model" also highlights the demands that are made on the mixing process. The art of mixing rubber lies in the breaking up of the various components and agglomerates and their even distribution throughout the polymer matrix in order to ensure the homogeneous quality of the compound.

As a rule, the various components cannot be merged in a single operation. This is particularly true of compounds that use fine-particle carbon blacks or natural rubber as their polymer base. The mixing process is generally divided into four stages:

• The cold raw polymer, which is fed into the mixing chamber in bale form, must be broken up in order to create sufficiently large surfaces for the incorporation of the fillers. Two contradirectional rotors inside the mixing chamber are used for this purpose.

Fig. 17: Using the so-called "spaghetti model" to illustrate the different sizes of the compound ingredients

#### Several operations

The shear forces generated by the rotors heat up the polymer, making it less viscous.

- The added fillers and plasticizers must be incorporated so that a coherent mass is created. During this stage, the polymer penetrates the gaps in the filler agglomerates and displaces the air. This part of the process is known as incorporation.
- The fillers, especially the carbon blacks, are available in the form of agglomerates that are broken up by the shear forces. This part of the process is known as dispersion.
- The broken-up fillers are then evenly distributed throughout the polymer matrix. This part of the process is known as distribution.

At every stage of the mixing process, changes occur in the surface properties, size, and degree of distribution of the additives as well as in the flowability of the polymer (as a result

# Temperature — Speed Plunger path - Energy Process parameters Time [min]

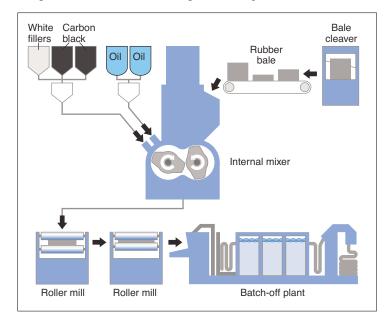
of the thermal processes) and, therefore, the flow characteristics of the materials being mixed. This is why the timing of the energy input is considered to be the "finger print" of the compound (Fig. 18). Continuous documentation of the most important process parameters - such as temperature, speed, time, and energy – are therefore used to monitor and ensure the quality of the compound. Internal mixers with intermeshing rotors are preferable for the production of high-quality technical elastomer components because they generally ensure a better quality of dispersion and allow for faster heat dissipation. This makes low-

From the provision of the raw materials to the delivery of the finished and tested compound, the production of a batch comprises a large

temperature mixing processes possible.

#### Continuous documentation

Fig. 19: Material flow in production



#### **Incorporation**

#### **Dispersion**

#### Distribution

Fig. 18: Time history of the process parameters during the mixing process

Cooling and

homogenization

number of different process stages. In order to ensure the steady flow of material, a variety of aggregates - from weighing equipment, bale cleavers, internal mixer, and roller mill to the batch-off plant – are needed (Fig. 19).

#### Using roller mills for homogenization

Roller mills generally have two rollers that are arranged one behind the other and run at different speeds. The temperature at both rollers can be controlled. The friction between the roller and the materials being mixed ensures that the flattened mixture (compound sheets) generally sticks to the slower front roller. The roller's first task is to cool down the compound, the temperature of which can be as high as 150°C at the end of the mixing process in the internal mixer. The roller also further homogenizes the compound. The mixing effect of the roller is based on several factors including the dispersion that occurs in the roller gap as a result of the different roller speeds. The distribution of the compound ingredients is reinforced by cutting the compound sheets and using auxiliary rollers, which are also known as stock blenders. The sheeting-out of the compound is influenced by the width of the roller gap, the friction, and the temperature. If the formulation requires it, temperature-sensitive curing agents and accelerators are added to the rolling mill after the cool-down phase. If the mixing line has two roller mills, there is more time for rolling during the internal mixer cycle. In order to ensure that processes can be reproduced and repeated, the roller process is automatically monitored and documented.

In exceptional cases, the compounds are subjected to very high shear forces in order to

break up filler agglomerates completely. In such cases, the compound moves through a very narrow roller gap (< 1 mm) with a simultaneously high level of friction in an extra roller mill. This improves the quality of the compound and is essential for compounds that require a high level of dispersion. This is the case for safety components, pressure seals, and lip seals.

#### Quality aspects and process control

The functional property and quality requirements for parts delivered to companies in the automotive and general industries have already increased significantly in recent years and are set to increase even more in the future. Legal guidelines and the fact that customers are demanding higher quality mean that continuous monitoring and documentation of the raw material quality, compounds, and processes is a necessity. Systematic advance quality planning ensures that all stages of the process – from the design phase to the development and production of the compound that is ready for series production – are carefully initiated and completed. During the development phase, for example, an FMEA (Failure Mode and Effects Analysis) is conducted in order to evaluate the compounds and any risks involved in their production.

In view of the fact that elastomer compounds are "customized materials", the manufacturers of technical elastomer products have to manufacture and manage a large number of different compounds (up to 1,000). A correspondingly large number of raw materials is also required for the production of the compounds. In order to ensure high-quality compounds, only raw materials from accepted

**Advance quality** planning

High rawmaterial quality

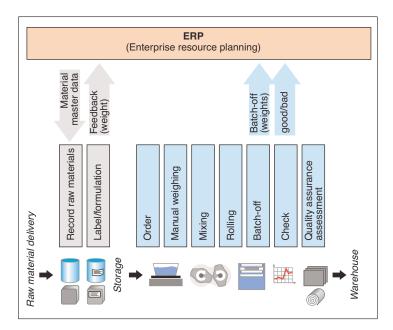


Fig. 20: Computer-assisted process for planning resources

**Organizing** mixing orders

and certified suppliers are used. In the production process, computer-controlled systems handle orders, manage raw materials, and control processes and quality (Fig. 20). In a large mixing plant with several mixing lines, every formulation is allocated to a particular mixing line in order to make the most of aggregate-specific strengths and to avoid frequent compound changes, associated set-up and cleaning times, and the risk of contamination. The order in which compounds are dealt with is arranged in such a way as to ensure:

- the largest possible batch sizes
- that formulations with similar raw materials are handled in succession
- that color changes can be avoided.

Optimization of the mixing processes and plants ensures reliable and stable mixing processes.

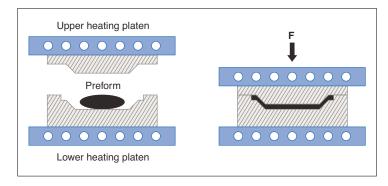
#### **Molding processes**

Rubber processing technology is a wide field that covers numerous processes from the processing of fluid latex to extrusion and molding procedures in self-contained tools and manually applied tank linings. The most widely used molding and curing methods for seals and technical molded parts are based on the production of components in self-contained tools.

#### **Compression molding**

Compression molding is one of the oldest methods of manufacturing technical elastomer components. This process requires a preform that is large enough to fill the mold for the component that is to be manufactured. The Barwell procedure has proven most effective for the manufacture of this type of preform. In this procedure, the rubber mass is pressed through a die and cut into very uniform pieces of the same weight by a rotating cutting appa-

Fig. 21: The principle of compression molding

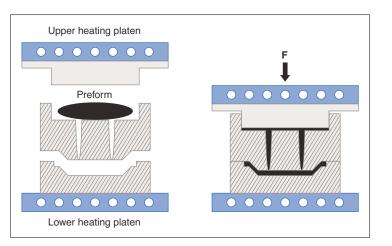


Long heating times

ratus. The preform is subsequently inserted into the component mold in the tool (mold cavity) and the press is closed. The heat generated by the heated platen is transferred to the molding compound, thereby triggering the curing process (Fig. 21). Compression molding requires relatively long heating times. The reason for this is that the preform must be heated from ambient temperature to the curing temperature, which is somewhere between 150 and 180°C. In view of the fact that elastomers are poor conductors of heat, this process can take several minutes, especially in the case of thickwalled components. In order to avoid air entrapments, the mold must be deventilated regularly by carefully opening the press several times during the curing process. Any excess material must also escape. The excess material forms a rubber skin (flash) in the mold parting surface of the two tool halves. This flash must be removed from the molded part in a separate finishing process after vulcanization.

#### **Transfer molding**

The transfer molding procedure is a refined version of compression molding and can essentially be performed using existing compression molding presses. Here, the upper half of the tool contains a cavity known as a "pot" into which the uncured compound is inserted in the form of a simple preform (Fig. 22). The pot in the upper half of the tool is connected to the mold cavity below by a series of narrow channels. The most important difference between compression and transfer molding is that in transfer molding, the mold cavity is already closed when the press process begins. When the press is closed, the tool pushes against an integral piston, thereby



pressing the elastomer compound into the mold cavity. Pressing the compound through the narrow channels ensures an intense exchange of heat between the compound and the wall of the tool. The flow speed also generates high frictional heat. This must be taken into account when developing the compound formulation, because additional frictional heat can lead to premature curing of the compound. The heating times for transfer molding are much shorter than those required for compression molding. Flash also forms in the transfer molding procedure. However, it is generally thinner than the flash created by compression molding. The transfer molding procedure allows molded parts to be manufactured within tight tolerance limits, which means that it is particularly good for the production of complex small parts.

#### **Injection molding**

Injection molding was used successfully in the plastics industry for several years before

Fig. 22: The principle of transfer molding

Shorter heating times

Molding using channels

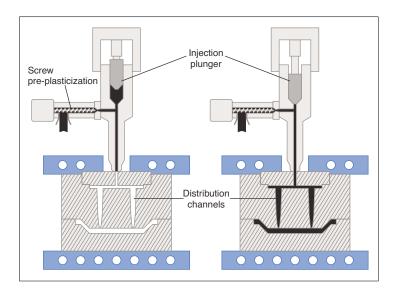


Fig. 23: The principle of injection molding

being introduced into the rubber industry. The structure of the tool used for injection molding is similar to that used for transfer molding with the exception that the individual mold cavities in the latter are connected to the gate (injection point) by means of channels. The molding process starts when the tool is closed. The pre-plasticized compound is then injected at high pressure through the injection nozzle into the distribution channels and on to the mold cavities (Fig. 23). The preferred type of injection molding used in the rubber industry features screw pre-plasticization and plunger injection. Here, the plasticization and injection procedures are kept separate, thereby ensuring that the full potential of every part of the plant can be exploited. As a result of pre-plasticization, the compound is almost at curing temperature when it enters the mold cavity. This means that the actual

Separate units

curing time in the injection molding process is shorter than that in all of the other processes mentioned here. However, as a result of the comparatively high investment costs associated with this process, injection molding is only suitable for larger production series.

#### production series

For larger

#### Other technologies

The problem of deflashing – or the avoidance of the formation of flashes in the first place – has led to the development of new processes and tools. The surface of the tool can, for example, be modified in such a way that air, but not elastomer, can escape from the mold cavity. This method is known as ready molding, or the flash-less process, and is particularly suitable for the manufacture of high-precision molded parts.

The combination of various molding processes has also resulted in the development of other processes. As the name suggests, the injection ready molding process, for example, combines the features of injection and ready molding. Injection compression molding is used to manufacture small, flat molded parts, especially O-rings. This process is based on the fact that a very tiny gap remains open when the tool is closed. The required pre-plasticized compound is then injected into this gap and the press is closed. Flat, high-precision molded parts that are largely flash-free can be manufactured using this process.

For the cold runner injection molding process, the injection channels are kept thermally separate from the tool. Thanks to the optimized design of the channel system and the fact that the temperature is kept at the

Injection ready molding

Injection compression molding

Cold runner injection molding

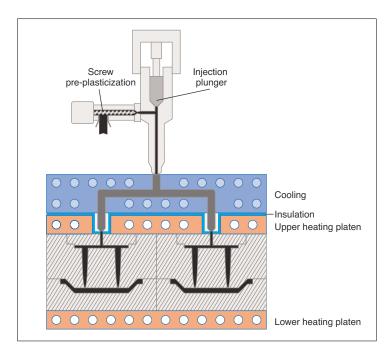


Fig. 24: The principle of cold runner injection molding

Time and material savings

right level, there is no loss of material as a result of previously cured sprues (Fig. 24). This saves huge amounts of material, which is particularly valuable when it comes to highquality compounds. By cleverly designing the channels, larger molded parts with small cross-sections can be manufactured. Compounds with very high free-flowing characteristics are required for this process. One positive side effect of these good free-flowing characteristics is the fact that they allow for an increase in injection speed. Not only does this save time, it also means that channels no longer have to be demolded and removed from the molded part. Cold runner injection molding can be combined with all molding

processes such as the conventional injection molding or the injection ready molding process, and allows for a high level of automation.

#### **Optimizing elastomer processing** procedures

Regardless of the curing process in question, it is vitally important to know the rheological properties of the compounds in order to be able to adjust process parameters to suit the material. Rheology concerns itself with the flow characteristics (viscosity) and shear behavior of materials. When it comes to optimizing production processes and saving costs in the rubber-processing industry, rheology and process simulation are inextricably linked. A knowledge of cross-linking reactions and their speeds helps the person developing the compound to determine the reaction kinetics and the chemical engineer to determine the ideal heating time. It also facilitates quality assurance in production. Rheological data is used for flow or injection simulations in injection molding in order to determine the dependency of the shear rate on viscosity and to use the results to calculate the elastic proportion of the elastomer stress. The simulation of injection processes is, therefore, an important aid when it comes to manufacturing defect-free components. For example, the flow front progression and the position of flow lines or the pressure required for selecting a suitable injection molding unit can all be calculated mathematically. This allows potential sources of error, such as entrapped air, to be identified and eliminated at an early stage.

Flow or injection simulations

#### Calculating the scorch index

By supplementing universal flow simulation programs with optimized material models that describe cure kinetics, both the scorch index (flow period, i.e. the time that elapses before the elastomer starts to cross-link) and the cross-link density during the injection molding of elastomer parts can be calculated.

An elastomer particle experiences fluctuating shear and elongation deformation between the time it is filled into the cylinder of the injection molding machine and the time it reaches its final position in the tool. The strong speed gradients at the side walls of the injection channel and the narrow temperature boundary layers must be taken into account for the simulation. Both special software packages and considerable computing power are needed to describe the complex, threedimensional flow processes (Fig. 25).

#### Considerable computing power

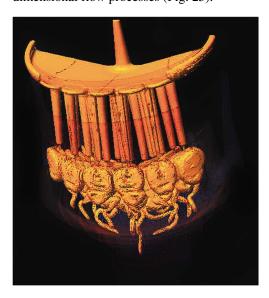


Fig. 25: Injection simulation of a conical spring illustrates complex flow processes.

Simulation of the compression molding process poses a particular challenge. In contrast to injection molding simulation, where the time-varying flow front within a rigid area (fixed walls of the mold cavity) needs to be calculated, not only does the flow front and consequently the parameters - change in the case of compression molding, but the two halves of the tool also move towards each other.

The advantage of all process simulations is that the parameters can be reliably altered, optimized, and checked on computer within days or hours. The findings can be channeled into the product and process design at an early stage of development. Simulation makes physical contexts and processes more transparent, thereby allowing the user to improve his/her understanding of the product or process - something that is not the case with exclusively experimental examinations. This means that optimization processes can be used in a targeted manner in places where the greatest potential is visible. It also means that maximum development results can be achieved at minimum expense and effort.

#### Early optimization

## **Testing elastomers**

Complex interrelationships

The main objectives of an elastomer test are to characterize the material, check that it functions as intended, and control the quality. In view of the fact that most elastomer properties depend on time and deformation, tests cannot cover all of the complex interrelationships between elastomer properties. In many cases, only limited statements can be made about the suitability of a product for the given operation. Consequently, in order to determine whether an elastomer is suitable for a specific application, it is vital not only to gather material data, but also to test the component in field trials.

#### **Testing during the production** process

An exact knowledge of the interrelationship between the formulation, the physical properties, and the way they change as a result of the effects of ageing is a prerequisite when it comes to improving the quality of the end product. In order to characterize elastomeric materials comprehensively, a large number of material properties are tested (Fig. 26). Determining the compression set, for example, provides information on the extent to which the elastic properties of elastomers are retained after long-term, consistent compressive deformation at a given temperature. In short, the compression set is one of the most important material characteristics that the product developer must know before his/her seal goes into operation. The quality of the elastomer compound can be determined and Ageing characteristics ■ in the air ■ in fluid media Stress relaxation, Component design Material characteristics creep Based on the optimized ■ Light and UV resistance ■ Tensile test material model Hardness Ozone resistance FEM calculations Elasticity Design optimizations Density **Dynamic properties**  Simulation of static and Strength Modulus, damping dynamic states of stress ■ Compression set ■ Durability (life) Abrasion Friction, wear Thermal properties ■ Low-temperature performance Process simulation Crystallinity Rheological and thermal **Processing characteristics**  Softening characteristics tool design Reactivity Flow characteristics Rheological data Demolding **Electrical properties**  PVT diagram Electrical conductivity characteristics Heat-conducting ■ Surface resistance Contamination properties properties Dielectric characteristics Other properties Diffusion Permeation

information gleaned on the suitability of the material for dynamic and static applications on the basis of the compression set. In addition to mechanical/technological properties such as density, hardness, tensile strength, and elongation at break, the physical interaction with contact media and chemical changes to the material caused by environmental influences are particularly relevant. However, data regarding the material's characteristics are not suitable for deciding whether a material is serviceable. Field trials regarding the influences of temperature and media over different periods of time are generally simulated in laboratory conditions. Modern component design procedures that are based on the FEM (Finite Element Method) and laboratory test runs under operating conditions allow for a comprehensive

Fig. 26: Overview of the testing methods applied at various stages of the production process

Field trials

#### Calculating the compression set

assessment of the function of components. Ideally, unambiguous statements about the serviceability of a material are based on the results of field trials featuring component prototypes.

#### **Estimating the working life**

Mechanical, thermal, and dynamic characteristic values are the basis for the development of material models, where not only the influences of the compound and the environment, but also the behavior of the material under dynamic load are taken into consideration. Unlike other materials such as metals and ceramics, there is no linear relationship between stress and strain in elastomers. In addition to this non-linear behavior, the stiffness of the material as a function of the deformation speed must be taken into account. Optimized material models - so-called hyperelastic material models – demonstrate good correlation between the experimental data and remain valid (Fig. 27) even in the event of considerable material deformation (>150%).

**Evaluating** ageing stability

Hyperelastic

material models

Evaluation of the ageing stability of elastomers is a particularly important criterion when it comes to assessing the durability of seals. The tests generally take the form of tensile tests on aged samples. In this regard, it is important to note that short-term and single-point determinations can always lead to misinterpretations. Observing ageing phenomena at different temperature and time intervals, on the other hand, can provide significantly more meaningful results and allow the long-term behavior of the elastomer to be estimated. Additional information that is obtained from component analyses and ageing

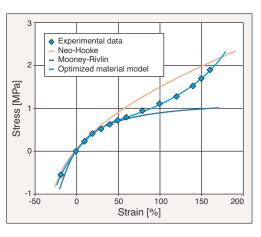


Fig. 27: A comparison of different material models and experimental data regarding stress-strain behavior

tests enhance numerical material models, thereby providing a comprehensive idea of the durability and, consequently, the working life of the elastomer seal.

#### **Component simulation using FEM**

The finite element method is used in industrial product development as a calculation procedure for solving complex problems relating to statics, strength, dynamics, and thermodynamics. In order to ensure the best possible design, the shortest possible development times, and top product quality when developing a technical elastomeric component, it is necessary to apply optimized methods of calculating the non-linear behavior and thus to illustrate the behavior of the material in the most accurate way possible.

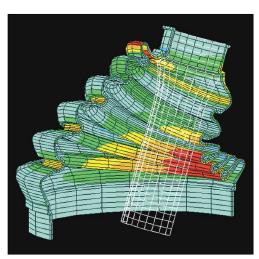
Non-linear FEM calculation models are indispensable when it comes to describing important phenomena such as the operating performance of elastomeric components, the process simulation in forming technology, or the cal-

Non-linear FEM model

#### Safeguarding the component function

Fig. 28: FEM calculation for an axle boot: the red areas indicate areas of extreme stress in the material

culated simulation of impact processes. On the one hand, simulation makes physical interrelationships more transparent for the user. On the other hand, taking account of non-linearities in the design process at an early stage allows the functions of the component to be reliably secured. Simulations based on FEM models, which describe the behavior of the material in exact terms, can make an important contribution in this regard and are gaining in importance. For example, the topology and form of components that will be subjected to mechanical loads can be optimized by taking minor stresses and strains into account.



#### **Example:** bellows

Bellows are a perfect example of how FEM calculations can be used with great success. Bellows that must be capable of accommodating large angular movements are used to seal the lubricant at axle joints. In addition to meeting elasticity requirements, it is vital that the components used in these applications

have long working lives. The loads applied to the axially symmetrical component are not themselves axially symmetrical. This is why a combination of axial and transverse loads must be taken into account during the calculation. The simulation reveals stress peaks in the component. These stress peaks can be reduced by adapting the design of the component accordingly or, to a certain extent, by optimizing the material. Changes in the component design have an enormous effect on the size of tensile and compressive stresses. In the case of bellows, this means that the maximum stress in the elastomer can be illustrated and subsequently reduced using simulations, which in turn means that the working life of the component can be extended by up to 10 percent compared with the conventional design (Fig. 28).

**Result:** extended working life

### **High-tech products** made of technical elastomers

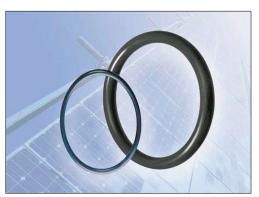
**Combinations** with other materials

Despite progress made in the various material groups, the special chemical, thermal, and mechanical properties of elastomers mean that they continue to be the basis of technical sealing solutions. Secure bonds between elastomers and metals, plastics, fabrics, or other materials mean that the material-specific properties of the various materials can be used to great advantage. Such bonds create multi-functional elements in the form of static or dynamic seals, molded parts, elastomeric composite parts, and much more.

Whether used in a static or a dynamic application, elastomer is always of decisive importance for the function, durability, and economic efficiency of the seal. Depending on the range of application, other special demands are made on the materials. The spectrum of available seals is broad and ranges from classic cord O-rings and radial shaft seals to components that simultaneously seal and provide vibration control. Some of these products are described below.

O-rings are predominantly used to provide a static seal between stationary machine parts and fluid or gaseous media. The sealing effect of the O-ring is based on the axial or radial deformation of its cross-section when it is installed. This deformation is achieved by designing the installation area accordingly. The resulting restoring force provides the contact pressure force necessary for the seal function.

This contact pressure force is also supported by the pressure of the media. As long as the Oring is installed correctly and the right material is chosen for the application, pressures of up to 1,000 bar and more can be sealed. Modern calculation methods can be used to simulate the deformation behavior of the O-ring during operation, thereby making it possible to enhance durability and optimize design. In addition to classic O-rings, various special versions that are capable of sealing complex component geometries are also available. O-rings that come into contact with hot water or steam during operation, e.g. in fittings, control valves, steam generators, feed pumps, solenoid valves, or in solar technology, are generally made of EPDM or HNBR (Fig. 29).



O-rings made of special EPDM compounds are characterized by improved long-time stability especially at high temperatures (up to 180°C in steam). In order to be able to use these O-ring materials in conjunction with drinking water, special approvals, which can vary from country to country, are required in addition.

Special parts for complex component geometries

Fig. 29: O-ring made of EPDM destined for use in solar technology

**O-rings** 

Fig. 30: Butterfly valve



#### **Butterfly valves**

Thousands upon thousands of butterfly valves or mechanically actuated shut-off valves for flow control are used in drinks, dairy, and bottling technology (Fig. 30). Simple and robust in design, they rarely malfunction. Butterfly valves must be capable of reliably withstanding pressures of up to 10 bar and flow speeds of up to 2.5 meters per second. The service life of seals is a decisive factor when it comes to the efficiency of butterfly valves. As long as the right material is selected, the seal will last for many thousands of switching cycles. In order to meet increasing technical requirements, the materials used must allow for low frictional torque when the valve is actuated and exhibit very good sealing behavior over the broadest possible operative range. Low elastomer relaxation also ensures that the valve seals exhibit high elastic resilience and therefore remain tight even after long cycles during which they are exposed to pressure (closed state).

Long-term tightness

> In addition to being resistant to the medium being sealed, seals for the food and beverage

industry must also be highly resistant to steam and aggressive detergents. In other words they must be suitable for use in CIP (cleaning in place) and SIP (sterilization in place) procedures. By virtue of the fact that they come into contact with foods, only harmless compound ingredients may be used in the elastomeric compounds for these applications. Moreover, these compound ingredients must comply with relevant legal guidelines (e.g. the recommendations of the BfR and FDA CFR 21 § 177.2600). New developments in this area include high-performance materials that are based on EPDM, HNBR, FKM, and in special cases, on FFKM. HNBR compounds, for example, combine very good mechanical strength values with good frictional characteristics. In view of the fact that HNBR is highly resistant to fats, waxes, and oils, these compounds are widely used in plants where these media have to be blocked or controlled. The operating temperature range for HNBR butterfly valve seals is  $-20^{\circ}$ C to  $+140^{\circ}$ C.

Diaphragms are always used in applications where components must be linked in a flexible way, spaces between components separated, and at the same time a tight separating wall ensured between them. In view of the wide range of possible diaphragm functions (transporting, adjusting, controlling, sealing, separating, storing), diaphragms can be used in applications in the fields of mechanical engineering, automotive technology, space travel, and medical technology. In the majority of cases, customized solutions are needed to meet varying requirements with regard to mechanical, thermal, and chemical loads. Diaphragms are used, for example, in pumps that transport fuel or lubricating media, or as New, highperformance materials

**Diaphragms** 

Customized solutions

Example: the twin-chamber system

control and sealing elements in valves for bottling plants. In addition to high media resistance, diaphragms must exhibit high abrasion resistance and good dynamic properties. The combination of tear strength (e.g. by using special fabrics) and flexibility allows diaphragms to achieve high to extremely high compressive strength and creep strength. Modern diaphragms that are used in actuators situated close to the engine translate even the tiniest pressure differentials into control and switching operations. Even under critical operating conditions – e.g. close to turbochargers or in blow-by gas flows that occur in the engine combustion process - diaphragms ensure long service lives and consistently reliable switching precision. One example of where diaphragms are used in actuators is the twin-chamber system, where they are used as a waste gate valve in vehicles (Fig. 31). This



Fig. 31: Twin-chamber system acting as a waste gate valve

system channels hot exhaust emissions past the turbocharger during cold starts and fullload operation. The twin-chamber system comprises two chambers working in the same direction that are separated by diaphragms. This system accelerates the light-off performance of the catalytic converter appreciably. In view of the fact that spark-ignition and diesel engines have different operating temperature ranges, different elastomer compounds must be used for the diaphragms.

Dynamic seals such as radial shaft seals (Simmerrings) are used to seal moving parts (e.g. rotating shafts). Among other things, they are used to seal crankshafts and camshafts in engines or in the drive train of passenger cars, commercial vehicles, agricultural machinery, and construction machinery, as well as in industrial gears, hydraulic power units, and washing machines. Dynamic seals used in industrial applications must last for up to 40,000 hours. Despite the use of friction-optimized materials, high shaft speeds and the resulting high circumferential speeds often cause extreme temperature increases at the sealing lip. In adverse conditions, this can lead to charring of the oil. The build up of charred oil residue at the sealing edge can ultimately result in leakage. This is why the elastomer used for radial shaft seals must be capable of withstanding such high temperatures. As a result of the increased use of modern synthetic lubricants in engines and gears, elastomers are also exposed to completely different chemical loads than is the case with conventional mineral oils. In short, the elastomers selected for these applications must exhibit a high resistance to this new generation of oil.

**Dynamic seals** 

Service life up to 40,000 hours

Fig. 32: Simmerring® with leakage sensor



#### Integral leakage sensor

In order to identify functional difficulties in good time, radial shaft seals can also be manufactured with additional functions such as a leakage sensor.

If the seal's sealing function diminishes once the product has reached a certain age, a leakage collector absorbs any fluid that escapes. An integral sensor identifies the leakage and sends a signal that indicates when the system will need to be serviced and the seal replaced (Fig. 32). This helps avoid unscheduled machine downtime.

New ground is also being broken in the fields of control and sensor technology in order to meet the requirements of low leakage rates (in the ppm range), reliability, and cost optimization. The combination of flexible printed circuit board technology and elastomers in the form of multi-functional sealing systems forms the basis of products that are capable of simultaneously sealing and transferring interference-free electric signals without the need for conventional cables (Fig. 33). This system consists of a static seal with integrated sensor, a plug, and a flexible printed circuit board that connects all the components to



Fig. 33: Sealing solutions with integral sensor, plug, and flexible printed circuit board can be manufactured for almost any kind of installation area.

form a sub-assembly. Without the need for boreholes, seals, and ducts, this multi-functional sealing system allows electrical signals to be sent into or out of an area filled with a medium and/or subject to pressure. Given the significant design freedom allowed by this system, it can be used in a wide range of applications in the automotive and consumer goods industries as well as for medical and telecommunications technology. The miniaturization of this sealing system and the fact that the flexible printed circuit board can be folded mean that this is a space-saving component that can be installed in even the smallest installation areas.

Bellows and dust boots are both used in the automotive, construction machinery, and food industries as well as for electrotechnical applications and medical technology. In cars, they are used to protect axles, transmission systems, shock absorbers, and steering systems. Drive shafts, propshafts, ball joints in tie rods, and stabilizers are all protected against the infiltration of dirt and moisture by special elastomeric bellows. Elastomeric bellows used in drive shafts also prevent the loss **Space-saving** solutions

Bellows and dust boots ...

... protect sensitive components

**Multi-functional** sealing systems

**Sealing systems** for hydraulic aggregates

of lubricants. Moreover, the bellows must be able to withstand excursions of up to 45° as well as exposure to high temperatures, media, and high local loads. The bellows have a flexible center part and two connectors. Appropriate connecting elements ensure that the component sits securely in place and guarantees the required tightness. The design of the bellows depends on the type of joint in question and the customers' specific requirements. As a result of the different loads applied to fixed and slip joints (inboard and outboard mounted), different elastomeric materials are needed to seal them. Joint shaft bellows for fixed joints are preferably made of thermoplastic elastomers (TPEs), while joint shaft bellows for slip joints are generally made of chloroprene rubbers (Fig. 34).

In view of the increased power density of hydraulic aggregates, the need for high-performance, leakage-free components can only be met by special sealing systems with long service lives. The sealing systems used in these applications generally comprise a combination of sealing elements that have been carefully selected to suit each other such as



Fig. 34: Elastic protective bellows for drive shafts

wipers, U-packings, guide strips, back-up rings, and rod seals. Sealing elements in the hydraulic cylinders of excavators, wheel bearings, and earth movers are exposed to particularly high loads. They must be capable of withstanding both heavy soiling from mud and dust, as well as major temperature fluctuations. In addition, the sealing system must not be damaged by high system pressures and pressure peaks in particular, or by the lateral forces exerted on the hydraulic cylinder. The latest generation of hydraulic seals exhibits high resilience even at extremely low temperatures, thereby allowing mobile hydraulic systems to perform fully without any noteworthy leakages in all climatic zones, even in the depths of winter (Fig. 35).

Another area of application in which technical elastomeric materials are used is vibration control technology. Vibrations occur in applications where starting torque, imbalances, or the influence of external forces and torque peaks play a role. The vibrations that are generated in this way not only create noise, they also subject components in the drive train to stress, thereby potentially shortening its ser-



Area of application: vibration control technology



Fig. 35: Sealing system for hvdraulic cylinders

# Hydro mounts as damping elements

Fig. 36: Engine mount with integral hydraulic damping (hydro mount)

vice life. Engines, gears, drive shafts, and couplings connected to downstream machines all affect each other mutually. In vehicles, vibrations can also be transmitted to the chassis and therefore to the entire vehicle body. which can lead to a reduction in ride comfort and even instability. The frequency range of the vibrations in the vehicle extends from approximately 1 Hz to over 1,000 Hz. In the stress field between insulation and damping, elastomeric components ensure that engines and the shafts in the drive trains run smoothly and with very little vibration and noise. When used as elastomeric decoupling elements with hydraulic damping properties, hydro mounts can, as a result of their special design, damp both low-frequency vibrations and isolate high-frequency excitation. Hydro mounts



(Fig. 36) that are used as cab bearings in agricultural and construction machinery improve user comfort and simultaneously create the conditions needed to meet legal guidelines on noise and vibrations as well as occupational safety guidelines.

### **Outlook**

In view of the continuously increasing demands made on sealing materials with regard to durability, friction, wear, and chemical and temperature resistance, as well as the increasingly strict specifications, it is vitally important for seal manufacturers to look closely at materials and the factors that influence their durability. This is the only way to ensure the development of modern elastomeric materials that can meet even the toughest functional requirements. As far as engines and gears are concerned, the trend is towards a broader usable temperature range (from  $-40^{\circ}$ C to  $+175^{\circ}$ C) and the use of fully synthetic lubricants. In addition to these requirements, both engines and gears have to meet stricter legal regulations. An example of such a regulation is the one relating to the "zero-emission vehicle", which stipulates that motor vehicles will in future no longer be permitted to emit any volatile hydrocarbon compounds.

The manufacture of customized polymers for specific applications allows for a considerable extension of the range of applications in which elastomer compounds can be used. For example, tailored ACM polymers were developed for the latest generation of shaft seals. The usable temperature range of these polymers (-40°C to +175°C) is 15°C wider than that of materials previously used in such applications, so that they consequently already meet the aforementioned requirements of the automotive industry. Special formulations allow for the development of new materials with improved wear resistance and ageing

Toughest functional requirements

Strict laws

Tailor-made elastomers

64 Outlook Outlook 65

Integration of additional functions

stability, which enhance the durability of the component.

As a result of the growing importance of electronics in general and the increased use of electric drives, new sealing concepts into which additional functions are integrated are being developed. These new designs render individual components superfluous, thereby reducing the required installation space, cutting weight, and ultimately simplifying installation for the user. For example, radial shaft seals with elastomeric encoder elements and active sensors for measuring vehicle speeds, especially in ABS systems, are already available. These seals feature a magnetizable elastomer layer with encoded sectors (see cover photo) that is attached either axially or radially to the outer side of the seal. A field sensor registers the varying intensities along the magnetic field and uses this data to provide a signal that gives information about the speed. In future, more consideration must be given to another aspect, namely electromagnetic shielding. The increase in the number of electric systems used in vehicles causes electromagnetic interference, which in turn can cause components to malfunction. The development of elastomers with increased electrical conductivity prevents electrostatic charge and interference caused by the mutual interaction of electrical components. Seals made of such electrically conductive elastomeric materials will in future be used in the field of sensor technology or electronic communications technology.

The development of hydrogen and fuel cell technology is considered to be an important pillar of future development. It is fervently hoped that these technologies will bring about a significant reduction in energy consumption and the emission of carbon dioxides in the field of transport and energy supply. However, the requirements for seals used in fuel cell systems are completely different to those for seals used in conventional combustion engines. Here, for example, gas permeation or very tough requirements regarding chemical purity play a very important role. Accordingly, the seals used in these systems must be impermeable to gas and exhibit high chemical resistance to the reaction products generated in the fuel cell.

The trend towards multi-functional sealing modules combined with modern processing technology makes it possible to produce components that are both delicate and complex. An in-depth understanding and knowledge of materials and the use of ultra-modern calculation processes such as FEM, and high-performance drawing and construction programs such as CAD will further accelerate the development of innovative elastomeric materials that meet the high requirements of quality, performance, and durability.

Fuel cell

Key to success: materials expertise

Electrically conductive elastomers

## **Glossary**

Agglomerates Condensed particles comprising a multitude of individual particles and measuring between approximately 50 and 100 nanometers (nm) in diameter.

Amorphous The adjective describes materials in which the atoms do not exhibit an arranged structure, but instead adhere to an irregular pattern. The adjective 'crystalline', on the other hand, is used to describe materials with a regular structure.

**Batch-off plant** Situated downstream of the mixing process, this plant is used to cool the sheeted-out elastomer compound.

**Brownian motion** The phenomenon that describes the thermally driven proper motion of molecules.

Creep The temperature- and time-dependent deformation of materials exposed to constant, long-term mechanical load.

Cross-linking Chemical reaction that is initiated by heat and/or pressure in which the polymer chains are linked to one another to obtain elastic properties.

Curing Process whereby rubber is transformed into a rubbery-elastic state as a result of a change in its chemical structure; also known as vulcanization.

**Diffusion** The equalization of differences in concentration between gaseous or dissolved substances in which particles move dependant on temperature from the area of higher concentration to the area of lower concentration.

**Elastic modulus** The tensile modulus of elasticity is an expression of the relationship between tensile stress and elongation. It describes the stiffness of the elastomer.

**Elastomers** Polymeric networks that are capable of absorbing large deformations in a reversible manner; cured rubber.

**Entropy** A thermodynamic quantity that describes the molecular mobility (disorder) of a system.

**Flash** A protruding edge of elastomer that forms during the molding procedure.

**FEM** Abbreviation of *Finite Element Method*; a numerical mathematical method.

FMEA Abbreviation of Failure Mode and Effects Analysis. The FMEA is an analytical method of identifying potential weak points.

Glass transition temperature The temperature at which polymers change from being flexible (the rubbery-elastic state) to being brittle (the energy-elastic state). This temperature varies from one polymer to another.

**Polymer** A macromolecule made of similar units (monomers). A polymer can be made of linear or branched molecules.

Rheology The branch of science that deals with the deformation and flow behavior of materials.

**Rubber** (Mayan language: cao = tree and ochu = tear) A collective term for non-cross-linked, elastic polymers.

**Scorch index** The flow period, i.e. the time that elapses prior to cross-linking of the elastomer.

**Simmerring**<sup>®</sup> Radial shaft seal, a trademark registered by Freudenberg.

**Stress relaxation** The decrease in stress over time under constant deformation and temperature.

**Thermoplastics** Plastics that can be plastically deformed under the influence of heat. Thermoplastics generally comprise polymers with linear or slightly branched chain molecules.

Thermosets Plastics that can no longer be molded once they have been cured.

**Torque** The product of an applied force and the distance between the point of application and the fulcrum.

Viscoelasticity The time-, temperature-, and speed-dependent elasticity of polymers, molten materials, or solids (plastics).

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# **Appendix**

#### Chemical nomenclature and sample applications

Abbre- viation	Chemical nomen- clature	Properties	Trade name	Application
NR	Natural rubber	High static and dynamic strength     Very low damping (= high elasticity)     Very good low-temperature performance     Low ageing, ozone, and oil resistance		Vibration dampers, ab- sorbers, engine mounts, machine mounts, and couplings in automobiles, mechanical engineering, and shipping
SBR	Styrene- butadiene rubber	Moderate elasticity     Very good abrasion and wear resistance     Moderate ageing resistance     No ozone/oil resistance	Buna SL®, Europrene®, Solprene®, Dunatex®	Molded parts, O-rings, diaphragms, absorbers, also used in automobile tires, conveyor belts, hoses, and floor cover- ings
CR	Chloro- prene rubber (polychloro- prene)	Good heat, weathering, and ozone resistance     Moderate oil resistance     Tendency to crystallization at T < 0 °C	Neoprene®, Baypren®	Bellows, dust boots, brake hoses, dampers in automobiles, applica- tions in the general and construction industries
EPDM	Ethylene- propylene- diene rubber (ethylene- propylene copolymer)	Very good heat and weathering behavior High ozone resistance Very good abrasion and wear resistance Very good low-temperature performance High hot water and steam resistance Not oil resistant	Dutral®, Nordel®, Buna EP®, Keltan®, Vistalon®	O-rings, molded parts, bearing elements in the food and beverage industry, also used to seal brake fluids in automobiles
NBR	Nitrile rubber	Good oil resistance     Good damping (as the acrylonitrile content increases)     Good abrasion and wear properties     Poor ozone resistance     Moderate ageing resistance     Moderate low-temperature properties (depends on the acrylonitrile content)	Perbunan®, Nipol®, Europrene®, Buna N®	Radial shaft seals, dampers, absorbers, diaphragms, hydraulic and pneumatic compo- nents, high-precision parts, O-rings for drive and electrical techno- logy, in the food indu- stry, also used to insu- late against the cold
IIR	Butyl rubber	Excellent heat, ozone, and weathering resistance     Chemical resistance to acids, hot water, and glycols     Impermeable to gas     Good low-temperature resistance     High damping, heavy dependency on temperature	Esso Butyl <sup>®</sup> , Polysar Butyl <sup>®</sup>	Diaphragms, O-rings for hot water and steam applications

ECO	Epichloro- hydrin	Good resistance to fuels, mineral oils, and greases	Hydrin®, Herclor®,	Diaphragms, molded parts, engine mounts in
	rubber	<ul><li>Impermeable to gas</li><li>Resistant to low temperatures</li></ul>	Epichlomer®	automobiles
HNBR	Hydrated nitrile rubber	Good oil and gasoline resistance like NBR, but with higher heat resistance     Good ageing resistance     Good abrasion and wear properties	Therban®, Zetpol®	Radial shaft seals, dampers, absorbers, dia- phragms, hydraulic and pneumatic components, high-precision parts, O- rings for drive and electri- cal technology, also used in sanitary and drinking water applications
ACM	Poly- acrylate rubber	Excellent heat, ozone, and ageing resistance     Very good oil resistance     High damping	Nipol AR®, Hytemp®, Noxtite®	Radial shaft seals, O-rings, flat gaskets, molded parts for gears in the automotive industry, also used in oil and coolant circuits
AEM	Ethylene- acrylate rubber	<ul> <li>Excellent heat and weathering resistance</li> <li>High ozone resistance</li> <li>High damping</li> <li>Moderate oil resistance</li> </ul>	Vamac <sup>®</sup>	Dampers, absorbers, flat gaskets for gears in the automotive industry, also used in oil and coolant circuits
FKM	Fluoro- rubber	Very good oil and chemical resistance     Extreme heat and weathe- ring resistance     Poor low-temperature properties below –20°C (exception: special types)	Viton®, Fluorel®, Tecnoflon®, Dai-El®, Noxtite®	Radial shaft seals, O-rings, diaphragms, molded parts, high- precision parts for engine applications, hydraulics, chemical and process engineering, aviation
FFKM	Perfluoro- elastomer	Excellent chemical resistance     Extreme heat and weathering resistance     Special types resistant to – 20°C	Kalrez®, Simriz®	Radial shaft seals, O-rings, diaphragms, molded parts, high- precision parts for chemical and process engineering, aerospace applications, also used to seal against aggres- sive media and steam
VMQ	Vinyl methyl polysilo- xane	Extreme heat resistance     Excellent low-temperature performance to -60°C     Low strength	Silopren®, Silastic®, Elastosil®	High-precision parts, O-rings, flat gaskets, diaphragms for medical applications
FVMQ	Fluoro- silicone rubber	High heat, ageing, ozone, and weathering resistance	Silastic®, FluorSilicon®	Molded parts, dia- phragms, etc., mainly used in the aviation industry
PVMQ	Phenyl- vinyl- methyl- polysiloxane	Very good low-temperature resistance, ozone-, UV- and weathering-resistant	GE-Sil <sup>®</sup> , Silastic <sup>®</sup> , Silopren <sup>®</sup> , Elastosil <sup>®</sup>	Molded parts, O-rings, diaphragms
AU	Polyester urethane rubber	Good ageing and ozone resistance     High tear strength and wear resistance	Adiprene®, Pellethan®	Pneumatic and hydraulic seals for general mecha- nical engineering appli- cations, agricultural and construction machinery, conveyor technology

#### 70 Appendix

#### Using elastomeric materials in a variety of sealing media

		R	SBR	CR	Ħ	EPDM	NBR	EC0	HNBR	ACM	AEM	FKM	FFKM	FFKM VMQ FVMQ	FVMQ	AU
Max. temperature [°C]	ature [°C]	08+	+100	+120	+130	+140	+120	+130	+150	+160	+150	+210	+230	+200	+175	06+
Permissible	Permissible minimum temp. [°C]	09-	-20	-40	-40	-40	90	-40	90	-30	-40	-20	-15	09-	09-	-30
	Engine oils	I	1	( <del>+</del> )	ı	1	+	+	+	‡	‡	‡	‡	÷	+	0
	Gear oils	I		<del>(</del> +	I	I	÷	+	+	‡	‡	‡	‡	÷	+	0
Mineral	Hypoid oils (EP oils)	I	1	(+)	1	I	(+)	+	+	‡	+	++	‡	(+)	+	0
Inoricants	ATF oils	_	1	(+)	1	_	(+)	+	+	‡	‡	‡	++	(+)	+	0
	Greases	_	-	(+)	1	-	+	+	+	‡	‡	‡	++	(+)	+	+
Synthetic	Polyalkylene glycols (PAG)	1	I	1	I	(+)	+	I	+	I	1	+	‡	1	+	0
lubricants	Poly-alpha- olefins (PA0)	_	I	0	ı	I	(+)	+	+	+	+	+	‡	(+)	+	0
Wineral	HLP in accordance with DIN 51524 Part 2	_	-	(+)	I	_	+	+	+	+	+	‡	‡	+	+	+
fluids	HLVP in accordance with DIN 51524 Part 3	_	I	(+)	I	_	+	+	+	+	+	‡	‡	+	+	+
Bio-	HETG rape seed oil	_	I	_	1	_	0	0	(+)	1	I	‡	++	0	+	0
degradable hydraulic	HEES synthetic ester	_	I	_	I	0	0	0	0	1	1	‡	‡	1	+	0
fluids	HEPG polyglycols	1	I	Ι	I	0	(+)	1	(+)	I	I	+	‡	1	+	1
Flame-	HFA group	-	1	1	1	1	+	_	+	1	1	1	++	1	1	1
resistant	HFB group	1	I	1	I	I	+	1	+	I	1	1	‡	1	I	I
hydraulic	HFC group	1	I	I	(+)	(+)	(+)	I	(+)	I	I	I	‡	I	1	I
Tiuids	HFD group	I	I	1	I	I	I	I	I	ļ	I	I	‡	I	I	I
	EL and L heating oil	_	1	0	1	_	(+)	(+)	(+)	1	0	‡	‡	0	+	1
	DOT3 /DOT4 brake fluid	0	0	_	(+)	++	I	_	I	I	I	I	‡	0	I	I
Other	Gasoline	_	1	-	1	_	(+)	+	(+)	1	1	+	‡	1	‡	1
media	Water	0	0	(+)	+	++	+	0	+	0	0	(+)	+	0	0	0
	Snds	0	0	(+)	(+)	++	+	0	+	1	1	(+)	‡	0	0	1
	CIP/SIP	-	1	1	1	+	Ι	0	(+)	1	1	+	+	0	1	1
	Air	0	0	+	+	‡	+	+	‡	‡	‡	‡	‡	I	‡	I
++ very good	++ very good, + good, (+) satisfactory, 0 moderate, - not suitable; special types may deviate from the information provided here	y, 0 mod	erate, – r	not suitab	le; speci	al types m	ay devia	te from t	he inform	ation pro	vided he	re				

#### The company behind this book

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Freudenberg Sealing Technologies is part of Freudenberg, the broadly diversified, internationally active and family-owned company. The technology specialist develops and manufactures a broad range of sealing technology solutions for its customers in the automotive, ancillary, and general industries. This range includes both customized solutions that are developed in close cooperation with the customer and globally standardized complete sealing packages. All of the world's major carmakers, their most important suppliers, and over 15,000 customers in general industry buy seals from Freudenberg.

Freudenberg has held a stake in the Japanese company NOK since 1960. The partners work closely and successfully within a global network on sealing technology solutions. They have founded a large number of joint ventures around the world and have adapted their company structures to complement one another. Milestones in the company's globalization include the establishment of Freudenberg-NOK General Partnership, which is based in Plymouth, USA, in 1989 and the NOK Freudenberg Asia Holding in 1996. Together, Freudenberg and NOK have over 50 production plants worldwide.

The Simmerring®, which was developed at Freudenberg by Prof. Walther Simmer in 1929, was the starting point for a range that today includes over 80,000 different sealing technology products. Down through the years, many of these products have been ground-breaking innovations. Today, seals assume additional functions, e.g. the transfer of signals to the brake or engine management system.

It is not possible to innovate in the field of sealing technology without an in-depth knowledge of elastomers. Freudenberg employs approximately 250 experts in its materials development units around the world. The company uses more than 1,600 different compounds and more than 850 different raw materials. State-of-the-art analysis methods and models developed within the company for calculating and simulating the behavior of materials are used to continuously enhance and refine Freudenberg's sealing products.