PROCESSING OF ELASTOMERIC MATERIALS

LÄROVERKET AB
Summary

We welcome students to a module where processing methods of elastomeric materials are discussed. Starting off with the mixing process of raw materials and continuing to describe all the different processing methods used to produce rubber products. Everything described for cured rubber as well as for thermoplastic elastomers.

Students may very well choose to study the module separately as an introduction to rubber technology and benefit from the fact that there is included a short description of polymers used in the rubber industry. The module deals with the following processing techniques of elastomeric materials.

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**Mixing**
In the mixing process an uncured compound is manufactured in order to be used for further processing into a rubber product.

**Textile treatment**
Reinforcing material has to be treated to obtain dimension stabilized products with good bonding between rubber and the reinforcing material.

**Calandering**
An important process to make flat sheeting, rubber coated fabrics as uncured products or as semi product parts.

**Spreading**
A technique for manufacturing thin rubber coated fabrics.

**Extrusion**
A technique for manufacturing long length products e.g. tubes or profiles which can be cured to final products or be used as parts in confectioned rubber products.

**Mould curing**
Main technologies for moulding rubber are compression, transfer and injection moulding and methods for post-processing of cured products.

**Rubber-metal bonding**
To achieve a good bonding between rubber and metal, the metal has to be degreased and treated with bonding agents before moulding or autoclave curing.

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**Vulcanization**
All different curing methods used to cure products shaped by the processes mentioned above.

**Latex processes**
The processes used for manufacturing of products from liquid rubber latex in contrast to the methods presented above, where dry rubber is used.

**Urethane rubber**
A presentation of the special processes used for manufacturing of products from liquid urethane rubber.

**Thermoplastic elastomers**
The following processing methods for thermoplastic elastomers are discussed; injection moulding, extrusion and some techniques for melt calandering and blow moulding.

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

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

After studying this module, the student has obtained a good overview and knowledge of different processing methods used for producing all kinds of products manufactured of cured rubber or thermoplastic elastomers. The student will also be able to choose a suitable technique that will optimize costs and quality.
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Introduction

Like the rubber materials, the processing of rubber has a long history. The history goes back to the beginning of the 1820’s. In England Thomas Hancock manufactured a machine for the mastication of natural rubber in order to achieve a consistency of material that could improve its process ability, this procedure is mastication and the technique is still valid.

The rubber polymers are high molecular weight materials, arranged in long chains and the processing is intended to mix rubber with particulate fillers, mostly consisting of very hard particles such as carbon black, silica as well as liquid softeners.

Most of the methods to process rubber materials require energy-consuming machinery operating under severe conditions. The rubber production can be divided into two basic steps. The first step consists of mixing, calendering and coating of fabrics. This step can be considered as a physical processing industry. Long runs of production are often most economically competitive and they make it possible to invest in advanced technical equipment and systems for process control. In this area of production semi finished products are manufactured for further processing to final products.

There are several methods and processes that aim to manufacture final products such as mould curing, extrusion or assembly of preshaped materials. This part of the rubber industry can be referred to as engineering industries where computerized and automated processes are dominating.

Manufacture of tyres is an excellent example showing this division in a processing part and a highly automated engineering manufacturing part.

However, a skill of craftsmanship is still a substantial and very important part of rubber production. By combining the many unique qualities that rubber material possesses with the craftsmanship maintained through more than a hundred years and constantly developed, modern techniques can be used for long line productions as well as for handmade special products.

The course aims to give the student a broad and in some parts deeper knowledge of different types of processing of rubber materials and thermoplastic elastomers with the results that the student after accomplished the course will:

- possess special knowledge as regarding processes of rubber and thermoplastic elastomers
- be able to assist in the mixing process
- be able to participate in the development process of existing and new processes and products in which rubber and thermoplastic elastomers makes an important part
- be able to solve rubber processing and manufacturing problems
1. Introduction to processing of rubber materials

The picture “Overview of polymers, elastomers and thermoplastics” shows that the elastomers are divided in one cross-linked (cured) group of materials – rubber - and one thermoplastic group - thermoplastic elastomers. Due to this difference the two groups of elastomers require different processes even if the properties of the ready products to some extend are comparable.

Rubber
- A compound is mixed of the polymer, fillers, softeners, curatives and other additives. (link to Raw materials and Compounds)
- The compound used are:
  - either preformed by calendering, coating on a fabric or by extrusion to become a component in a final product
  - or by calendering or extrusion given the right shape for the final product
  - or for filling the cavity in a mould.
- For many products like tyres, hoses and belts the preformed parts have to be assembled to the shape of the final product.
- The product is then cured at a temperature of 140 - 200 °C to receive its requested final properties. Through the curing which is the crosslinking process, the rubber compound properties are changed from a plastic to an elastic state. In some cases the curing is done online at the same time as the forming of the product i.e. for extruded products like sealing profiles and cables.
- The cured product may in some cases pass a post-process e.g. post-curing or surface treatment.
- Finally a quality control operation is done.
Thermoplastic elastomers

- The material is normally supplied ready mixed directly from the raw material supplier.
- The shaping of the products is done by heating the material to a temperature above the melting point. After the forming process the product is cooled to room temperature. That is when the material will receive its properties.
- The main processes used are:
  - Calendering
  - Extrusion
  - Moulding by injection in a cavity
- The final product has to pass a quality control operation.

1.2 Special features of the processing of rubber

- The processing properties are highly depended on the composition of the rubber compound.
- To achieve the expected properties of a product a proper mixing procedure is essential.
- The final properties for the rubber product is achieved when the curing process is taking place at a temperature of normally 140 – 200 °C whereby the rubber is cross-linked and obtains its elastic state.
- The elastomer and hence the compound is viscous, therefore processing (e.g. extrusion or moulding) of the uncured compound is improved at elevated temperature. The processing temperature often goes up to 100 - 110 °C and is thereby coming close to the curing temperature. The compound must be compounded so that scorching (start of curing reaction) will not start at the processing temperatures.
- At the same time the curing reaction – being depended on time and temperature - must be as fast as possible to admit short curing time and contribute to a high productivity.

2. Rubber, a short description of rubbers

2.1 History of rubber

The history of the very earliest rubber materials is shrouded in the mists of time. It is said, however, that Columbus, during his second voyage to the Americas (1493 - 1496), saw the natives of Hispaniola (Haiti) playing a game with elastic balls. What was unusual with the balls was that they bounced far better than the balls that were used in Europe. Recent research has shown that the people of the West Indies and parts of Central and South America were acquainted with and used rubber for various purposes long before the rest of the world had any knowledge of this strange substance.
As early as in the beginning of the 16th century, bits of rubber were taken to Spain, but for a long time rubber was merely regarded as a curiosity. A very long time would pass before scientists and entrepreneurs were able to introduce this rubber material into the general stock of usable materials, but the seed was sown of what would eventually become a global rubber industry.

In spite of the fact that the development of rubber technology took place in the 16th, 17th and 18th centuries, and rather slowly, a very fundamental problem remained to be solved; the finding of a remedy for the one great disadvantage of rubber, that is its tendency to became hard and brittle in the cold and soft and sticky the heat.

2.1.1 The discovery of vulcanisation

During the first half of the 19th century, several attempts had been made in Germany, Great Britain and the USA to improve the properties of rubber so that it was stable in shape, dry and flexible instead of being soft and sticky.

It was the American, Charles Nelson Goodyear, who in 1839 after many years of unsuccessful attempts and great personal sacrifice discovered that if you mixed a small amount of sulphur into the rubber and heated it then it obtained the desired properties.

This basic discovery, which Goodyear patented in 1844, is what is known today as vulcanisation (also called curing).

Vulcanisation is a process in which rubber, by a change of its chemical structure, using cross-linking, is transformed to an elastic state.

Vulcanisation improves and amplifies the elastic properties of rubber over a greater temperature range.

The discovery of vulcanisation is so vitally important that the rubber industry would never have been able to develop to what it is today without it.

2.1.2 Rubber materials

If we say that the date of birth of the rubber industry is simultaneous with the discovery of vulcanisation, then the hundred years between the 1830’s and the 1930’s saw a large number of discoveries, inventions and improvements that were of great importance for the vulcanisation process.

Activators and accelerators were developed which made the cross-linking reaction faster. Ageing protection was developed to prevent degradation of the
rubber materials. **Reinforcing fillers**, such as carbon black, were developed to improve wear resistance and other mechanical properties.

This development was encouraged by the newly established automobile industry at the end of the 1800’s and its ever-increasing demand for rubber products such as tyres and inner tubes. The pneumatic tyre invented in 1888 by **J. B. Dunlop** lead to the manufacturing of one of the most important rubber products from the point of view of production volumes.

At the beginning of the 20th century, natural rubber was very expensive, which of course stimulated interest in trying to produce elastomers artificially, i.e. synthetic rubber. Researchers in Germany, Great Britain, France and Russia worked intensely during this period to produce synthetic rubber materials.

The work lead to some success, but because the price of natural rubber dropped dramatically in the years before and during the First World War (1914 – 1918), the work was held up or was at least considerably reduced in scope.

![Development of prices for natural rubber.](image)

*Prices of NR*

The development of the combustion engine and the central role it played in the development of the automobile meant that there was a continued huge demand that was demonstrated by the fact that the demand for rubber was increased tenfold between 1910 and 1940.

During the 1920’s, research was once again started which made great progress with regard to the understanding of what the molecular structure of rubber looked like and how the use of catalysts could speed up the polymerization process.

Two new, extremely important, synthetic elastomers saw the light of day at the end of the 1920’s - two copolymers that have had enormous importance for the automobile industry among others. One of the new materials was **styrene-butadiene rubber (SBR)**, which is now the most common type of synthetic rubber.
of all with an annual world consumption of 8 – 9 Mtons and with its primary use in car tyres. The other material was nitrile-butadiene rubber (NBR) which has good resistance against fuels and oils and which was greatly in demand by the automobile manufacturers. In 1995, the world consumption of NBR was approximately 650 000 tons.

The consumption of synthetic elastomers in 1930 was approximately 100 000 tonnes, which was the equivalent of almost 10 % of the total consumption of rubber in the world. During the Second World War, the production of rubber, primarily SBR, increased dramatically due to the West being cut-off from supplies of rubber from what now is Malaysia.

The blockade, which among other things threatened the mobility of the American Armed Forces, lead to the American Government deciding to quickly increase the production capacity of SBR. From 1943 to 1945, the capacity was increased from 30 000 tons to 900 000 tons. This must be regarded as a formidable engineering feat.

At the end of the Second World War, in addition to natural rubber there were also six commercial types of synthetic elastomers available, there are 30 - 35 different types of elastomers, depending on the criteria used for the classification.

2.2 Classifications, different types of rubber

There are plenty of different rubber types available but still the largest single type used is natural rubber (NR), produced of latex from the tree Hevea Brasiliensis. The synthetic types of polymers, mainly manufactured from oil, have been developed either to replace or to be used together with NR or to make polymers with properties superior of NR in special areas, typically with better high temperature resistance, better outdoor resistance and/or resistance to fuels and oils.
A common classification of different types of rubber is:
- General purpose elastomers
- Special purpose elastomers
- Speciality elastomers

### 2.2.1 General purpose elastomers

General purpose elastomers comprise:
- Natural rubber (NR)
- Polyisoprene rubber (IR)
- Styrene-butadiene rubber (SBR)
- Butadiene rubber (BR)

These types have good physical properties, good process ability and compatibility, are generally economical and are typical polymers used in tyres and mechanical rubber goods with demand for good abrasion resistance and tensile properties. General purpose types constitute the largest volume of polymer used.

![World rubber consumption](image)

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2.2.2 Special purpose elastomers

Special purpose elastomers comprise:

- Ethylene-propylene rubber (EPM and EPDM)
- Butyl rubber (IIR)
- Chloroprene rubber (CR)
- Acrylonitrile-butadiene rubber or Nitrile rubber (NBR)

They have all unique properties which cannot be matched by the general purpose types and are very important for manufacturing of industrial and automotive rubber products.

2.2.3 Speciality elastomers

The **Speciality elastomers** are a great number of polymers with very special properties, in many cases of great importance for the automotive-, aircraft-, space- and offshore industries. Some of these polymers are:

- Chlorosulfonated Polyethylene (CSM)
- Acrylic Rubber (ACM)
- Silicone Rubber (PMQ/PV/MQ/VMQ)
- Floursilicone Rubber (FPQ)
- Fluor elastomers (FPM/FFKM/FEPM)
- Urethane Rubber (AU/EU)
- Epichlorohydrine Rubber (CO/ECO/GECO)

2.3 Terminology

There are a large number of different types of elastomers. Each type of elastomer has its own special properties, which makes it suitable for various products. These properties influence the designer’s choice of type of elastomer and also affect how the elastomer is processed in the factory.

The properties can be modified to a certain extent by various ingredients in the formula and by the processing. In the manufacturing, the process must therefore be carefully controlled in order for the desired properties to be obtained. In these sections, the properties and the terminology used will be described.
2.3.1 Properties

Ageing resistance

All elastomeric materials age more or less with time. The ageing process can be divided into two main reactions, thermal and oxidative degradation.

Cold stiffening

When an elastomer is cooled down its rigidity increases and when it reaches what is known as the glass transition temperature, the elastomer becomes completely rigid and brittle. When heated however the elastomer regains its original properties.

There are several methods of determining the elastomer’s cold stiffening properties like TR-test and Gehman test. The brittle point is the temperature at which the rubber becomes as hard as glass, brittle and breaks when impacted.

Compression set

By compression set is meant the permanent set that is obtained when the load is removed from a compressed test piece. The compression set is given as a percentage of the deformation. An acceptable, low, compression set is important for products which are used for sealing purposes.

Creep

Creep is a slow accumulative deformation in the rubber when subjected to a constant load. Classification can be done for both elongation and compression and it is given as a percentage of the original unloaded dimension.

Damping

If a solid rubber ball is dropped onto a hard surface, it will not bounce back to the initial height due to the damping effect of the rubber. Internal friction and the kinetic energy, which is transformed to heat in the rubber, cause the damping. The damping is normally measured by determining the rebound elasticity using an impact pendulum and it is expressed as a percentage of the initial height of the drop.

Discolouration

An elastomeric material that comes in contact with a surface painted in a light colour can discolour that material. The discolouration is caused by antioxidants and softeners migrating from the rubber and entering adjacent surfaces, such as plastic materials or painted surfaces. The effect can be accelerated by sunlight.
Fatigue resistance

Certain elastomeric products are subjected to dynamic elongation or bending fatigue. The fatigue resistance is different for different types of elastomer, but can also be affected by the composition of the compound.

Fatigue can be tested using test pieces for elongation or bending. The result is given as the number of cycles at break. The property is often tested using the products themselves.

Hardness

The hardness of an elastomeric material is a measure of its rigidity or modulus. This property is the one most often used in the classification of elastomers in specifications, etc. The measurement of hardness is carried out by pressing a measuring probe in the form of a truncated cone or a hemisphere into the rubber. A measurement is made of how far the measuring probe can penetrate into the rubber and the result is given in Shore A degrees or IRHD (International Rubber Hardness Degrees).

Ozone resistance

Certain rubber materials, i.e. those with double bonds in the main molecular chain, are prone to reaction with ozone. That leads to formation of typical cracks which run perpendicular to the material’s direction of extension. The ozone attack increases with increased elongation of the elastomeric material.

Resistance to oils, solvents and chemicals

Different types of elastomers have different resistances to oils, solvents and chemicals. These resistances can, to a certain extent, also be affected by the compound.

The resistance is often tested by immersing the test pieces in the particular medium in question, e.g. oil. After a certain length of time, sometimes at an elevated temperature, the changes in weight and volume are measured, and sometimes also changes in mechanical properties.
Stress relaxation

A deformed rubber test piece, whether elongated or compressed, resists the deformation. The opposing force decreases however with time and that is called stress relaxation.

The opposing force decreases faster at first and thereafter at a decreasing rate, and then finally after a long time it often decreases quickly again when the life cycle of the material is at its end.

Stress relaxation can be divided into two different processes, physical and chemical relaxation.

Tear strength

Tear strength is an elastomeric material’s resistance to continuous tearing and it is given in N per mm test piece thickness and determined by the tensile testing of a test piece with a nick in it. A good tear resistance is related to good abrasion resistance and is an important property for products.

Tensile strength and elongation at break

The tensile strength at break is a measurement of the material’s strength and is given in MPa.

The elongation is the material’s elongation at breaking point in %. Both the properties are determined by tensile testing of a dumbbell test piece.

Rubber materials produce, as opposed to metals, a non-linear load/deformation curve.

Standard materials normally have a tensile strength of 7 - 20 MPa and an elongation at break of 200 - 500 %

Tensile stress

The tensile stress of an elastomeric material is a measurement of the elastomers resistance to extension. Tensile stress is normally given for a particular elongation, 100 or 300 % and is given in MPa.

Tension set

The tension set is the resulting permanent deformation after the removal of the load from an extended test piece and it is given as a percentage of the elongation.

Wear resistance - abrasion

Wear resistance is, together with elasticity, the property that makes rubber so useful. With regard to abrasion, rubber is superior to the majority of materials, even steel. This is due to the fact that rubber is soft and has a damping effect.

Testing of abrasion is difficult to carry out in the laboratory and it is also difficult to achieve a correlation with what happens in real applications. This is why nearly all abrasion resistance testing is carried out on finished products.
2.3.2 Processes

Curing or vulcanisation

Curing or vulcanisation is a process where the elastomer compound is transformed from a yielding plastic material into an elastic material. This is done by a sparse network of bonds being formed between the molecules of the elastomer material. Normally sulphur is used as a curing agent.

Calendering

A process where you squeeze the elastomer compound into a film (< 0.25 mm), foil (0.25 - 2 mm) or sheeting (> 2 mm).

Compression moulding

A process where the elastomer compound is inserted into a mould cavity, the mould is closed and the products are cured. Just like making waffles.

Extrusion

A process which shapes the elastomer compound into long strips, e.g. sealing strips.
Injection moulding

A process where an injection cylinder is used to inject the elastomer compound into a closed mould, in which the product is cured.

Mixing

Mixing is the process whereby the elastomers are mixed with ingredients such as fillers, softeners, activators, antidegrading agents, processing aids, accelerators and curing agents.

2.3.3 Materials

Accelerators

Compounding materials that facilitate and speed up the vulcanisation. The accelerators consist of complex organic compounds.

Activators

Compounding materials which facilitate (activate) the vulcanisation reaction.

Antidegradant

Compounding materials which protect against oxidation, e.g. antioxidants, antiozonants and waxes.

Crystallisation

A phenomenon which takes place in certain types of elastomers with highly regular molecules. At lower temperatures, the molecular chains arrange themselves close together and the material hardens.

When the temperature is increased the material regains its previous properties. This applies primarily to natural rubber and chloroprene rubber.

Curing agents

Compounding materials which form cross-links during vulcanisation. The most common are sulphur and peroxides, but also resins and metal oxides are used.
Fillers
Compounding materials which dilute the polymer. There are normally two types of fillers, reinforcing and non-reinforcing.

- **Reinforcing fillers** increase the strength of the rubber materials. They consist of materials with small size particles as reinforcing fillers. The most common are carbon black and silica.
- **Non-reinforcing fillers** are pure diluents which reduce the price and also impair the mechanical properties. The most common filler is whiting.

Glass transition temperature
The middle point of the temperature interval where a rubber material is transformed from an elastic material to a hard and brittle glass-like material.

PHR
Parts Per Hundred Rubber (PHR). This is used for the calculation of formulas. The compound ingredients are given as parts per 100 by weight of the rubber polymer.

<table>
<thead>
<tr>
<th>Basic formula:</th>
<th>PHR (Parts per Hundred Rubber)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rubber</td>
<td>100</td>
</tr>
<tr>
<td>Carbon Black</td>
<td>50</td>
</tr>
<tr>
<td>Oil</td>
<td>30</td>
</tr>
<tr>
<td>Curing agent</td>
<td>2</td>
</tr>
<tr>
<td>Activator</td>
<td>5</td>
</tr>
<tr>
<td>Antidegrant</td>
<td>2</td>
</tr>
<tr>
<td>Accelerator</td>
<td>1</td>
</tr>
</tbody>
</table>

Plasticisers (Softeners)
Compounding materials which reduce the hardness of a rubber material, e.g. oil.

Processing aids
Compounding materials which facilitate the process, e.g. dispersing agents, peptizing agents, mould lubricant, etc.
2.4 What is a Polymer?

*Overview of polymers, elastomers and plastics*

**Polymers**

A polymer consists of large molecules. The word polymer is made up of the elements “poly”, which means many, and “mer”, which means unit or part. A single “mer” is called a monomer. The polymer consists of many monomers in long chains. The chains of polymers can be straight and/or branched.

A polymer is produced by the polymerisation of one or more types of monomers. If the polymer consists of only one type of monomer it is called a homopolymer and if it contains different types of monomers it is called a copolymer.

**Thermoplastics**

We usually differentiate between two types of thermoplastic materials, thermoplastics and thermosets. The thermoplastics mainly contain linear and/or branched polymers, while the thermosets, after shaping, contain crosslinked molecules in a three dimensional network.

A thermoplastic is shaped in a mould while the molten compound is being subjected to pressure at an elevated temperature. The shape of the product is then fixed as it cools down in the mould. The thermoplastic article can be reshaped if it is reheated again. The Greek word termos means heat and the word plastic means mouldable. Thermoplastics are not modified chemically during shaping.

A thermoset hardens during shaping through chemical reactions, which lead to molecule enlargement and the forming of crosslinks into a three dimensional network. A thermoset cannot be reshaped by recycling the pressure and heat process. After the curing reaction, the thermoset are in fact not remeltable or soluble in solvents. At sufficiently high temperatures the molecules are instead degraded by molecular scission.
Elastomers

The elastomers include materials with considerable elastic elongation, that is to say materials which at room temperature can normally be extended to at least double their original lengths without rupturing and which when the load is removed return to almost their original lengths.

This property can be found in polymers with easily moveable chains of molecules. In order for the molecular chains, after straightening out, that is to say after deformation, to be able to return to their original configuration after the load has been removed, they must be attached to each other at certain points, which is why the structure can be described as a three dimensional network.

A hard elastomer which can be an elastomer with so much filler that it cannot be elongated to twice its length is normally still considered to be an elastomer. Rubber with lots of sulphur so called ebonite, is normally considered to be rubber, but should in fact belong to the thermosets. Ebonite has so many crosslinks that a rigid network is created.

Rubber

An elastomer, in which structural transformation has been achieved by chemical crosslinking, is called rubber. The process by which the crosslinks are formed (often with the aid of sulphur) is called curing. Rubber is processed and shaped in its molten state. The shaped product vulcanises when heated and is transformed into an elastic state. In order for a polymer to become rubber, the polymer is required to be in its molten state at the temperature of use. In the vulcanisation process, a sparse network of crosslinks is then formed. A rubber is thus a sparsely crosslinked molten polymer.

![The network structure in a sulphur cured rubber material](image)

Thermoplastic elastomers

Elastomers, in which structural transformation is achieved by physical cohesion forces, are called thermoplastic elastomers and given the abbreviation TPE.
Thermoplastic elastomers normally consist of two polymers, a polymer (thermoplastic in nature) which is frozen at the temperature of use and a polymer (rubber) that is in its molten state at the temperature of use. The frozen polymer forms bonds using physical cohesive forces. By heating, the frozen polymer is molten and a product can be shaped. The thermoplastic elastomers can therefore be processed and shaped in the same way as the thermoplastics.

![A typical structure of a thermoplastic elastomer](image)

### 2.5 Field of applications

The automotive industry is the biggest user of rubber products. Besides the tyres a modern car maybe has up to 1000 rubber parts of various sizes and they amount in average to 4.25 % of the total weight of the car.

The distribution of rubber products in different sectors shows in diagram:

![Usage of Rubber](image)

**Usage of rubber**

In value a very rough estimation is:
- Tyres 50 %
- Automotive 25 %
- Other industry/consumer 25 %

Typical products made out of each of the polymers are shown in the appendix 1.
For each rubber types the chemical structure, general information, properties and applications are presented in appendix 1. The values given in the appendix 2 applies to average compounds and intends to give general outlines for selection of rubber type for a specific purpose.

3. Thermoplastic elastomer

These materials that combine elastomeric properties with many of the attributes of thermoplastics have been available to industry for over twenty years. A wide acceptance of thermoplastic elastomers has taken place due to growing experience backed by convincing case studies in many sectors of industrial activity; new-generation materials have been developed to meet the demands of ever more discriminating customers.

Today the world wide consumption is around 1 M tons.

The materials have a structural transformation achieved by physical cohesion forces and are called **thermoplastic elastomers** and given the abbreviation **TPE**.

*Thermosplastic elastomers products (Photo Flexys)*

*Thermoplastic elastomers are normally supplied as granulates in bags and can be used directly to feed extruders and injection moulding machines. (Photo Flexys)*
Thermoplastic elastomers normally consist of two polymers, a polymer (thermoplastic in nature) which is frozen at the temperature of use and a polymer (rubber) that is in its molten state at the temperature of use. The frozen polymer forms bonds using physical cohesive forces. By heating, the frozen polymer is molten and a product can be shaped. The thermoplastic elastomers can therefore be processed and shaped in the same way as the thermoplastics.

A typical structure of a thermoplastic elastomer

### 3.1 Classification

To describe elastomer types, there are designations of two up to four letter combinations, for example SBR for styrenebutadiene elastomer. These designations for thermoplastic elastomers shown in the adjacent table are:

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPE</td>
<td>General group designation</td>
</tr>
<tr>
<td>TPA</td>
<td>Polyamide</td>
</tr>
<tr>
<td>TEEE</td>
<td>Polyester</td>
</tr>
<tr>
<td>TPO</td>
<td>Olefines</td>
</tr>
<tr>
<td>TPS</td>
<td>Styrenics</td>
</tr>
<tr>
<td>TPU</td>
<td>Urethanes</td>
</tr>
<tr>
<td>TPV</td>
<td>Alloy of a thermoplastic and cured rubber</td>
</tr>
<tr>
<td>TPZ</td>
<td>Other TPE types</td>
</tr>
</tbody>
</table>
### Example of designations used for common TPE-types

<table>
<thead>
<tr>
<th>Designation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPO(EPDM+PP)</td>
<td>Uncured EPDM blended with PP</td>
</tr>
<tr>
<td>TPS-SBS</td>
<td>Styrene-Butadiene-Styrene block polymer</td>
</tr>
<tr>
<td>TPS-SEBS</td>
<td>Styrene-Ethene-Butene-Styrene block polymer</td>
</tr>
<tr>
<td>TPV(EPDM+PP)</td>
<td>Cured EPDM blended with PP</td>
</tr>
<tr>
<td>TP-(IIR+PP)</td>
<td>Cured IIR blended with PP</td>
</tr>
<tr>
<td>TPZ(NBR+PVC)</td>
<td>Cured NBR blended with PVC</td>
</tr>
</tbody>
</table>

**The structure of a thermoplastic elastomeric alloy**

**Schematic diagram of thermoplastic polyurethane**
3.2 Properties

In the table below, data of the most important types of thermoplastic elastomers are shown. For each type there are also a great number of varieties, whose properties can vary over a wide range. The properties of the thermoplastic elastomers usually vary more between different hardnesses, than do those of vulcanised rubber. The values given must therefore be seen as a kind of average.

**Table of the properties of thermoplastic elastomers**

<table>
<thead>
<tr>
<th>TYPE</th>
<th>Mechanical properties</th>
<th>Operating temperature</th>
<th>Resistance (Rating)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hardness IRHD</td>
<td>Tensile strength MPa</td>
<td>Wear rating</td>
</tr>
<tr>
<td>TPS-SBS (SiS)</td>
<td>30-95</td>
<td>5-15</td>
<td>3</td>
</tr>
<tr>
<td>TPS-SEBS</td>
<td>30-96</td>
<td>5-20</td>
<td>2</td>
</tr>
<tr>
<td>TPV-(NBR+PP)</td>
<td>55-95</td>
<td>5-20</td>
<td>3</td>
</tr>
<tr>
<td>TPV-(EPDM+PP)</td>
<td>55-95</td>
<td>5-20</td>
<td>3</td>
</tr>
<tr>
<td>TPV-(NBR+PP)</td>
<td>80-95</td>
<td>10-20</td>
<td>3</td>
</tr>
<tr>
<td>TPV-(IR+PP)</td>
<td>60-95</td>
<td>3,5-5</td>
<td>3</td>
</tr>
<tr>
<td>TPU</td>
<td>70-95</td>
<td>25-50</td>
<td>5</td>
</tr>
<tr>
<td>TEE4</td>
<td>90-97</td>
<td>20-40</td>
<td>5</td>
</tr>
<tr>
<td>TPA</td>
<td>75-97</td>
<td>20-40</td>
<td>3</td>
</tr>
</tbody>
</table>

*The values refer to conceptualised types. Rating: 1 = poor, 2 = fair, 3 = good, 4 = very good, 5 = excellent.
3.3 Field of application

The different TPE materials are used in a number of areas, depending on the properties, as:

- Components in cars
- Components in electrical products
- Shoes
- Hoses
- Toys

General information’s, properties and applications for the different types are presented in the appendix 3.

4. Processing methods for rubber materials

4.1 Mixing

The mixing department plays a central role in the operation of a rubber factory. This is where the elastomer compounds are produced which are then shaped and vulcanised into final products. The basic principles for mixing rubber materials have not changed very much during the approximately 150 years that the rubber industry has been in existence. But of course the processes have been extensively developed regarding process control, automation and improvements in machinery constructions.

Synthetic types of rubber have supplemented natural rubber but the compounding techniques have remained roughly the same. Comprehensive development and modernisation has however taken place concerning the capacity and control of machines as well as with environmental improvements. This is clearly seen if you compare an older with a newer mixing department.
Except for the mixer a mixing line contains of silos and containers for different ingredients like (carbon black, mineral fillers, oil etc.) as well as automatic weighing systems and mills or an extruder (for handling the compound after being dumped from the mixer) and a cooling line.

4.1.1 Raw materials

Receiving raw materials

- Polymers and other raw materials for rubber compounds are delivered to the mixing department in different packaging and sizes.
- On arrival, the quantity and packaging are inspected and the goods are identified.
- The supplier’s certificate of analysis is examined and compared with the internal inspection specification.
- Normally, a random sample is drawn and analysis of some significant property which can be compared to the supplier’s certificate is carried out.
- This is done in order to verify the supplier’s information and also to determine the actual status of the goods.
- For example, the viscosity and moisture content may have altered during transport and storage.
- After having been approved in the goods receiving inspection, the raw material is made available for mixing.
- If, however, the goods are rejected, an investigation is carried out and eventually a complaint is made to the supplier of the material.
Example of packaging units for raw materials

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Packaging unit</th>
<th>Amount/package</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rubber polymers</td>
<td>Pallet</td>
<td>500 – 1 000 kg</td>
</tr>
<tr>
<td>Carbon black</td>
<td>Steel container/large bag/tanker</td>
<td>500 – 1 000 kg</td>
</tr>
<tr>
<td>Filler</td>
<td>Bag/large bag</td>
<td>25 – 20 000 kg</td>
</tr>
<tr>
<td>Plasticisers</td>
<td>Drum/tanker</td>
<td>200 – 20 000 kg</td>
</tr>
<tr>
<td>Other</td>
<td>Bag/large bag</td>
<td>25 – 1 000 kg</td>
</tr>
</tbody>
</table>

Except for the mixer a mixing line contains of silos and containers for different ingredients like (carbon black, mineral fillers, oil etc.) as well as automatic weighing systems and mills or an extruder (for handling the compound after being dumped from the mixer) and a cooling line.

Storing of raw materials

- The rubber industry stores large amounts of raw materials for varying lengths of time. In certain cases, it could be a question of several months.
- The reasons for this could be the need to stockpile various materials, to achieve discounts for volume purchases, to achieve fully loaded truck transport etc. or to allow for anticipated price increases.
- It is very important that the raw materials are stored properly. Otherwise problems can occur during mixing and curing.
- Indoor storage in dry, evenly heated premises provide the best conditions.
- A normal room temperature is quite sufficient for most raw materials with the exception of crystallising polymers and high viscous oils.
- Crystallising polymers, as for example natural rubber and polyisoprene, become very hard during transport and storage in low temperatures.
- It takes approximately 14 days for a rubber pallet to reach the ambient temperature of the environment.
- Transportation of rubber can therefore be carried out in cold temperatures without crystallisation occurring, but often the storage time in cold temperatures can be considerably longer.
- Crystallisation is a reversible process but decrystallisation takes place first at roughly 35 - 40 °C.
- A well-equipped mixing department has therefore a special heating room set up in order to carry out decrystallisation at least during the cold half of the year in the Northern hemisphere.

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• Due to the poor heat conductivity of rubber and its packaging, the time in the heating room could be anything between 1 and 2 weeks.
• Highly viscous oils must sometimes be pre-heated in order to achieve flow through pipes and pumps.
• At delivery, the oil is heated and it must then be stored in a heated tank.
• The heating of raw materials described here can also be helpful in the mixing process itself. The process becomes somewhat shorter and the strains on the mixer considerably lower.

Weighing

• The first operation in the mixing process is the weighing of the ingredients according to the formula.
• Rubber polymers are weighed directly from the pallet on a conveyor belt scale. The bales weigh 25 to 35 kg and should be handled with a lifting device.
• Carbon black, oil and even non-black fillers are automatically weighed in the course of the mixing, usually with one or two batches being weighed beforehand and stored temporarily in a weighing hopper or filler pipe.
• These raw materials are retrieved via a mechanical or pneumatic transport system from storage tanks and silos.
• Ingredients in smaller amounts are weighed manually in buckets or thermoplastic bags in advance according to the planned requirements. Automatic weighing systems are also used for environmental purpose.
• The bags are made of a thermoplastic material, which will melt at the actual mixing temperature. The bag does not then need to be emptied when it is added and this ensures that its contents end up in the right place that is to say in the compound.
• The accuracy of weighing should be in order of ± 1 %.
• To ensure that the scales are weighing correctly, a calibration scheme is required.
• A system is required for registration and follows up of scales and measuring equipment used in the production to ensure their performance.
4.1.2 Equipments

There are three categories of mixers:

- Mixing mills
- Internal mixers
- Continuous mixers

Powerful electrical motors are required in order to operate a mixer and a lot of heat is produced when the rubber is milled. All the various types of mixers are therefore equipped with systems for the circulation of the cooling water. In modern plants, the heat of the cooling water is used for heating the premises and the hot tap water.

**Mixing mill**

- The mixing mill is the oldest and simplest type of mixing machine. In laboratory work, small mixing mills are very useful for mixing and processing rubber compounds, but in the industrial process mixing mill operation is dirty, time consuming and provides a poor working environment.
- Mixing mill operation is therefore only used to a limited extent. When mixing on a mill, the polymer is placed between the **rolls** and is processed until it forms an even belt around one of the rolls with a certain amount of excess compound where the rolls meet.
- Then fillers, **plasticizers** and other chemicals are gradually added to the “mixing zone” between the rolls. Some chemicals fall down into the tray underneath the mill and must then be fed into the mixing mill again. Finally, when all the non-curative ingredients have been incorporated, curing agents and accelerators are added.
- The total mixing time often amounts to at least 30 minutes for a batch size of approximately 100 kg.

*Mixing mill with an overhead mixer (equipment placed over a mill, where the compound is turned around by mechanical means). (Photo Werner & Pfeiderer)*
**Internal mixers**

- This type of machinery consists of two **rotors** in an enclosed chamber. The rotors are shaped so that they produce a kneading effect while at the same time the chamber ensures that all the materials which are added remain in place.
- The wear from fillers (mainly carbon black) used in the compound, in the chamber is very hard while the surfaces have to be applied with a welding surface like stellites or iron and cobalt-based compounds.
- Basically two different types of internal mixers are used either with tangential rotors or with intermeshing rotors. There are also a number of variations of these two. The other parts of the machine e.g. **ram** (plunger), **feed hopper** and **drop door** are often the same.
- The two types differ somewhat in the mixing techniques discussed in the following, but in general the types with intermeshing rotors are preferred for heat sensitive compounds. Cross sections of the two types are shown in the figure below.

*Cross section Internal mixer:*

*B with intermeshing rotors (Intmix type).*
In the bottom of the chamber there is a hatch or discharge door, which can be opened and at the top there is a plunger (ram) which can be lowered and raised between the open and closed positions. This movement is done pneumatically or hydraulically and these operating media can also be used in order to provide extra pressure on the plunger in its closed position.

When mixing, the ingredients are added through the feeding door at the top or through separate pipes (e.g. carbon black, mineral fillers and plasticizers) directly into the mixing chamber in roughly the same order as when mixing on an open mill. The number of revolutions per minute of the rotors can be varied even while the mixing cycle is in progress. The number of revolutions per minute can, for example, be increased when plasticizers are incorporated since the viscosity and the degree of dispersion would otherwise normally decrease.

The process can be speeded up by using the plunger pressure and increasing the number of revolutions thus often reducing the time it takes to mix a batch to under 5 minutes. The most common size of internal mixer produces approximately 250 kg per batch, but sizes producing from 40 to over 400 kg per batch are used in different areas of the rubber industry.

When the compound is completed, the hot mix is discharged through the bottom hatch in the form of a lump. It needs to be quickly sheeted out and cooled in order to avoiding scorch.

The two most common techniques are:

The compound is dumped into an extruder, often a pinextruder in which the compound will be forced through a wide die and then formed to a continue sheet.

The compound is dumped on a two-roll mill with an over head mixer (stockblender) in order to improve the final homogenisation of the compound and to form a sheet.

In order to increase the capacity, two open mills can be placed in tandem.

In both cases, the approximately 80 cm wide length of rubber is transported via conveyor equipment to a cooling section.
• Antitack agent is sprayed on both sides of the sheet of the compound. The operation takes several minutes and during that time cold air is blown over the rubber.
• After this procedure, the rubber can be regarded as cooled and can be placed on pallets for further transportation.

![Cooling tunnel for mixed compound (Photo WMI EPE Holland)](image)

**Continuous mixers**

• In the 1960’s it was considered appropriate to introduce a new mixing technique with continuous manufacture instead of producing one batch at a time. A specially designed type of extruder was developed for this purpose.
• When mixing, the raw materials are fed continuously. All solid materials must be finely pulverised into granulates in order to ensure even dosage. An ingeniously designed screw then provides the processing that is required in order to obtain a homogenous mixture.
• The method has been shown to work for certain formulas and where the production of large series could justify the difficult start-up operations.
• In general however, it could be considered that the method failed due to the severe limitations in its performance and the higher costs for the finely granulated raw materials.

**4.1.3 Mixing techniques**

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

1. **Viscosity reduction**
2. **Incorporation**
3. **Distributive mixing**
4. **Dispersive mixing**
• Each of these steps occur in practise mostly simultaneously, as for example it is not unusual that part of the filler has been dispersed before the incorporation is fulfilled.
• Viscosity reduction is called mastication and is a mechanical breakdown of the polymer to achieve the expected plasticity.
• Incorporation is the step when solid and fluid ingredients are incorporated into the polymer by mechanical work or by diffusion into the polymer. High temperature speeds up the incorporation.
• Distribution is the step when the particles incorporated into the polymer are evenly distributed in the whole batch.
• The dispersion aims to break up the agglomerates in fine particle fillers e.g. carbon black to give as big contact area between polymer and filler as possible. This step is in most cases the most difficult one in the whole mixing process.

![A mixing machine with a feed conveyor belt.](Photo Trelleborg Forsheda)

4.1.4 Processing variables

The compounds are usually mixed in two or more steps in internal mixers:

1. The polymer, carbon black, other fillers, plasticizers and so-called small chemicals e.g. stearic acid, zinc oxide and antioxidants are added.
2. The curing additives normally sulphur and accelerators are added.

This technique means that the first step may be mixed at a high speed on the rotors which will generate a high temperature. This will improve the dispersion and the mixing time will decrease. The second step however may, as the fillers already are dispersed in the polymer, be mixed at a lower temperature and scorching is therefore avoided.
The mixing result of a fixed compound can be influenced by a number of factors of which following are the most important:

- **Fill factor in percentage** - tells us how much of the chamber’s volume that are filled with the compound. Depending on the compound a fill factor somewhere between 55 and 75 % is regarded as normal.
- **Ram pressure** – for most types of machines the ram pressure is in the size of 0.2 to 0.6 MPa. An increased ram pressure will shorten the mixing time and increase the temperature.
- **Rotor speed** - an increased rpm will increase the shear rate and improve the dispersion.
- **Dumping** - is controlled by one of the criteria mixing time, temperature or energy or a combination of these. Computer programs have been developed for online calculation of the viscous properties of the compound and thereby control the dumping.

### 4.1.5 Batch control

Each mixing batch is checked in order to make sure that no defective material is processed further. The inspection is carried out on a sample drawn from each batch or per volume of the rubber compound, which is proportional to a batch. First of all the viscosity and vulcanisation rate is tested in a **rheometer** and compared with a standard which provides minimum and maximum tolerances.

A rheometer is used to establish the viscosity and curing data of rubber compounds

This test is the most definitive for ensuring that everything is in order. Other tests which are performed with greater or less frequency are the measurements of viscosity, density, hardness and tensile strength of vulcanised rubber.

The measurement of dispersion is a test which will have greater use in the future. New modern equipment has been developed which is based on advanced video and computer technology. This test will probably be able to replace the time consuming tensile test. Development is now towards carrying out the testing of rubber compounds as an integrated part of the manufacturing process itself.

To ensure correct measurements, calibration of the testing equipment has to be done according to a set schedule. The calibration should be done by a qualified laboratory, operated by the factory itself, an independent qualified laboratory or a customer assigned laboratory. The laboratory has to have a certificate including permission to calibrate the specific devices. Commercial/independent laboratories should be accredited according to ISO/IEC Guide 25 or corresponding national institution.

If a qualified laboratory is not available for a specific device, the manufacturer has the qualification to do the calibration.
Standard PC software is available for registration of test equipment and for making schedules for the calibration intervals.

Photo Trelleborg Försheda, Alf Gustavsson

Diagram of a curometer (Flexys)

4.1.6 Maintenance

A mixing line may consist of equipment for the automatic weighing of carbon black and non-black fillers, scales, a 200 litre internal mixer, two 84 inch mills and a cooling tunnel. This line is expected to be available at all time, and represent a high economic investment.
To achieve a good performance a thorough preventive maintenance system must be operated.

- All operators at the line have to do careful cleaning of the equipment to avoid impurities in the compounds. They must observe leakage or other defects.
- Lubrication and change of oil is to be carried out according to the manufacturers’ instructions.
- Periodic check ups, made by specialists such as electricians and mechanics, to control.
- Periodic check ups, made by specialists such as electricians and mechanics, to control parts affected by wear and to make preventive replacement of critical parts.
- Periodic service made by the machine supplier, when equipment such as scales and measuring devices are calibrated. Measuring of the wear in the mixing chamber and on the rotors is carried out at the same time to ensure correct mixing action.

To fulfil the requirements of ISO and QS certifications, a scheme with preventive maintenance of all machines and other equipment must be established.

\[
No \text{ part of a mixing line is stronger than its weakest link.}
\]

4.1.7 References

- www.tut.fi/plastics/tyreschool (modul 1)
- Practical Rubber Compounding (C. W. Evans)
- Rubber Products Manufacturing Technology (Bhowmick, Hall, Benarey)
- Rubber (Läroverket AB)
- Rubber Technologist’s Handbook (J R White & S K De)

4.2 Textile treatment

Many rubber products contain reinforcements, mostly textiles or metals, in order to increase the capacity of the rubber to carry loads. Reinforcement makes the product more rigid in one or two dimensions. Such products are sometimes called flexible composites.

It is important to obtain good adhesion between the reinforcing material and the rubber. For textile materials, adhesion is obtained by impregnating the fibres using an adhesive solution. This is often done together with a hot stretching, which fixes the fibres so that they are not excessively elongated during curing or if the final product is used at a high temperature.
Special **adhesive solutions** can also be used for metals, but for metal wire, such as steel cord, a brass coating is often used on the steel in combination with an **adhesive agent** in the rubber.

**Example of products containing reinforcement materials of textile and/or steel cord:**

- Tyres of various kinds
- Conveyor belts
- V-belts and driving belts
- Hoses
- Tracks for scooters and tracked vehicles
- Foot wear
- Protective clothing
- Rubber sheeting
- Flexible couplings
- Pneumatic springs
- Membranes

### 4.2.1 Reinforcing materials

Natural fibres like cotton consists of short fibres, 10 - 50 mm long, called staple fibres, while the synthetic fibres are very long and called filament fibres.

Textile fibres are spun into yarns containing many thin fibres. These yarns are then twisted to obtain increased strength and fatigue. Often two or several yarns are twisted together to a **cord**. The cord can be used directly for reinforcement in rubber products or can be woven into fabrics of different kinds. One type of fabric that is often used is tyre cord fabric, which has all its strength in the longitudinal direction of the warp while the weft yarns are few and weak.

The function of the weft in a tyre cord fabric is to hold the weave together until it is coated with rubber.

Steel cord also consists of two or more twisted steel wires.

The following types of textile and steel wire reinforcing materials are used in the rubber industry.

- **Cotton** – which was the first textile material used, but today mostly replaced by synthetic types of textile.
- **Rayon** – a regenerated fibre of cellulose which has a wide use both in tyre and industrial rubber products.
- **Polyamide** – (also known under DuPont trade name nylon) a fibre with higher strength and better fatigue properties than rayon.
- **Polyester** – is more and more becoming a standard reinforcing textile material in rubber products.
• **Polyaramide** – (also known under DuPont trade name Kevlar) has very high tensile strength, very high rigidity and very low elongation at break. The greatest disadvantage is its high price. As polyaramide has a strength equal to steel and has a low density, it may very well replace steel cord in some applications.

• **Glass fibre** - has high tensile strength, high rigidity and resists high temperatures, but it has poor bending fatigue strength. It has a limited usage i.e. in hose and membranes.

• **Steel wire** - in the form of steel cord is used today in the belts of radial passenger tyres. It is also used in truck tyres in the carcass. Steel has a high tensile strength, high rigidity and a good resistance to high temperature. In addition to its use in tyres it is also used for hoses, driving belts and conveyor belts.

The properties of the different reinforcing materials are presented in the table below.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Rayon</th>
<th>Polyamide</th>
<th>Polyester</th>
<th>Glass</th>
<th>Steel</th>
<th>Polyaramide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength, cN/Tex</td>
<td>42</td>
<td>71</td>
<td>67</td>
<td>68</td>
<td>32</td>
<td>152</td>
</tr>
<tr>
<td>Tensile strength, GPa</td>
<td>0,64</td>
<td>0,81</td>
<td>0,92</td>
<td>1,73</td>
<td>2,5</td>
<td>2,19</td>
</tr>
<tr>
<td>Force at spec elongation, cN/Tex</td>
<td>530</td>
<td>360</td>
<td>560</td>
<td>1420</td>
<td>670</td>
<td>1950</td>
</tr>
<tr>
<td>Tenacity, GPa</td>
<td>8</td>
<td>4,1</td>
<td>7,8</td>
<td>36</td>
<td>52</td>
<td>28</td>
</tr>
<tr>
<td>Elongation, %</td>
<td>13</td>
<td>21</td>
<td>15</td>
<td>4,8</td>
<td>2,0</td>
<td>4,0</td>
</tr>
<tr>
<td>Bending fatigue, min</td>
<td>400</td>
<td>2000</td>
<td>800</td>
<td>15</td>
<td>-</td>
<td>400</td>
</tr>
<tr>
<td>Max operating temp, °C</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>350</td>
<td>300</td>
<td>200</td>
</tr>
<tr>
<td>Dencity, g/cm³</td>
<td>1,52</td>
<td>1,14</td>
<td>1,38</td>
<td>2,54</td>
<td>7,8</td>
<td>1,44</td>
</tr>
<tr>
<td>Relative price per kg</td>
<td>1,0</td>
<td>1,3</td>
<td>1,1</td>
<td>2,2</td>
<td>1,2</td>
<td>7,6</td>
</tr>
</tbody>
</table>

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4.2.2 Treatment for textile adhesion

To achieve good bonding between textile materials and rubber, textiles like rayon, polyamide and polyester is treated with a solution based on rubber latex.

It is called the RFL-bonding system and is an impregnation in which the fabric is dipped into a solution with the active components:

- Resorcinol
- Formaldehyde
- Latex

The type of latex used is chosen to fit the polymer in the compound to be used for coating the fabric in a later process. The common types of latex used is NR, SBR and VP (vinyl pyridine) when the fabric should be used for coating with rubber based on General Purpose type polymer. Dip solutions based on CR latex are used for i.e. oil resistant products where the fabric may be coated with NBR or CR as well as butyl rubber (IIR) latex for coating with IIR or EPDM.

The dip coating is forming a film on the textile after impregnation, drying and curing during which the resorcinol and the formaldehyde form a resin.

The film is chemically linking the surface of the textile with the rubber, and is even levelling the big difference in module between rubber and textile. The factors affecting the performance of RFL dip solutions are mainly:

- Resorcinol/formaldehyde ratio
- Conditions of resin formation
- pH of the resin solution
- Type of latex
- Latex/resin ratio
- Total solid in the solution

The mixing of the dip solution is made by solving resorcinol formaldehyde in water and after that adding diluted latex. The pH of the solution is controlled by adding sodium hydroxide. The whole mixing cycle is a sensitive process made in several steps and includes a maturation time (aging time).

The expected bonding level is beside the composition of the dip heavily depending on mixing temperature and maturation time which can vary from a very short time up to 24 hours, but in general about 8 hours.

The first diagram shows the bonding, tested by H-test, as function of mixing temperature. The second diagram shows the bonding as function of the relation between latex and resorcinol-formaldehyde.
The impregnation is done, in connection with the hot stretching. The fabric is brought through a bath containing the dip solution and followed by passage through rolls, a scraping blade and a vacuum pump to make it possible to control the amount of dip solution on the fabric.
The process variables used in the process are:

- **Exposition time** – controls how much dip solution is soaked up by the textile.
- **Pulling force** – low pulling force results in deeper penetration of the dip solution to the fabric.
- **Roll pressure** and **vacuum pressure** contribute to achieving of an even, specified amount of dip solution in the fabric.

The amount of dip solution and the penetration in the textile affect beside the bonding even strength and fatigue properties. Normal **dip pick up** for synthetic fibres is 4 - 5 % and a penetration depth of about 2 filaments.

Drying and curing is then made in a heat chamber and here the result is depending on correct temperature, exposition time and pulling force.

### 4.2.3 Hot stretching

All reinforced rubber products are finally vulcanized and it is essential that the reinforcing material is dimensionally stable during the curing process.

Polyamide and polyester are thermoplastic and liable to shrink when heated. The tendency to shrink is minimized by heat setting, meaning that the fibre is heated to a temperature higher than the expected process temperature. As all textile fibres will growth if they are subjected to tension stress they even have to be stretched during the heat setting which will increase the modulus and reduce tendency to growth.

To achieve the optimal effect of this fixation of the fibres, it is made on the finished textile structure as cord fabric for tyres, cord for V-belts, fabrics for conveyor belts.
etc. The common process is to combine the impregnation for bonding and the fixation in hot stretch equipment as in the figure above.

By the fixation, hot stretching, following advantages are received:

- Improved tensile strength
- Increased modulus
- Decreased "plastic" stretching
- Increased length

The process variables used are:

- Temperature
- Exposition time
- Pulling force

They will affect the textiles properties as follows:

<table>
<thead>
<tr>
<th>Properties affected</th>
<th>Increasing of process variables</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>decrease</td>
</tr>
<tr>
<td>Modulus</td>
<td>increase</td>
</tr>
<tr>
<td>Shrinkage</td>
<td>decrease</td>
</tr>
<tr>
<td>Creep</td>
<td>decrease</td>
</tr>
<tr>
<td>Fatigue</td>
<td>increase</td>
</tr>
</tbody>
</table>

- **Temperature** is normally kept as high as possible, i.e. 225 °C for polyamide and 240 °C for polyester.
- **Exposition time** affects the properties in same direction as the temperature, and the two variables are optimized in combination
- **Pulling force** applied to the textile results in a stretching which for polyamide ≈ 9 % and for polyester ≈ 3 %

### 4.2.4 References

- Rubber Manufacturing Technology (Bhowmick, Hall & Benarey)
- Rubber Technology (John S. Dick)
- Rubber (Läroverket AB)
4.3 Calendering

Calendering is a process where rubber compound is formed to a continuous sheet or coated on a fabric. This is done by feeding the rubber compound to one or several on each other following roll gaps.

- Two rolls built together in a frame, forms one gap and is called a **two-roll calendar**.
- Three rolls forms two gaps and is called **three-roll calendar**.
- Four rolls forms three gaps and is called **four-roll calendar**.

The figures show different configurations of the rolls in a calender and also give examples of the use of respective machine.
An example of “A state of the art” calendar is the four-roll Z-calender, normally used for double side coating of textile cord with rubber.
Calendering is used in the manufacturing of a multitude of products either for rubber coatings of fabrics or for the preparation of sheet products.

Rubber coating is an important process of manufacturing i.e. tyres, conveyor belts, hoses and footwear.

Sheet preparation is used for the same products as above and for all kind of technical rubber sheeting. Perfect sheets up to 2 mm thickness can be produced without air inclusions. For thicker sheets a combination of an extruder and a calendar is used, so called roller head calendar.

4.3.1 Machinery

In a calender the rolls are mounted in a frame made of cast iron with high tensile strength. The rolls have a diameter from around 200 to 750 mm and face length from 250 to 2 500 mm (the smallest are laboratory calenders) and are manufactured for highest concentricity, resistance to deformation and with high quality surface finish.

To allow a good temperature control the modern calenders have peripherally drilled passages for heating or cooling, while older machines often are heated or cold from steam/water in the central bore.

The drive of a calender is normally a thyristor controlled direct current drive which can be either a separate motor for each roll or one central motor with the torque transmitted between the rolls via gears.

Roll deflextion and methods of correction

A main problem with calendering is that the rolls bend because of deformation due to the pressure from the rubber between the gaps. This means that thickness variations of the calendered material will occur.

In order to compensate for this deflection, different methods have been developed.

The most common methods are:

Roll camber (roll crown)

Camber is when one or several rolls are ground so that they have different diameters in the centre and at the ends to compensate for the deflection. This functions well if you run products which use roughly the same material and thickness.

The figure shows an exaggerated example of roll camber. In the upper figure the rolls are unloaded and in the bottom figure they are loaded with rubber between the rolls.

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**Cross axis (crossed rolls)**

Cross axis means that one or several rolls can be displaced laterally in relation to each other, thereby leaving a larger gap at the ends of the rolls than in the middle. The advantage with this method is that the degree of compensation can be varied.

The figure shows a view of crossed rolls with cross sections taken at the centre and at one end of the roll.

**Roll bending**

Roll bending means that a load is placed on the shaft spindles of the roll which cancels the bending force in the middle of the roll. This produces bending moments with the roll’s bearings as the points of support its two arms. With this method, continuously variable compensation can also be obtained.
Roller die calender

For certain types of manufacturing a roller die are used, where an extruder with a wide die applied directly to the nip of a two roll calender.

With that process, up to about 15 mm thick sheeting can be calendered with the result of low porosity due to trapped air as no bank of rubber is built up by the feeding to the calendar.

Other lines where roller dies equipments are used:
- Batch off lines after an internal mixer
- Production of innerliner for tyres
- Production of treads for conveyer belts
- Production of sheets of fiber loaded compounds for V-belts

4.3.2 Peripherial equipment

Feeding device

The rubber compound has to be heated, normally up to 80 – 100 °C before it is fed to the calendar. That is done either on a series of mills or by the use of a cold feed extruder.

An internal mixer may be used on line with the calender where the last mixing step is done and the rubber transferred to a cutting mill and fed to the calender.

The use of mills, 2 - 4 in line, where the compound is moved from mill to mill and then cut off in a strip from the last mill and fed to the calender is the oldest technique, but still used to quite an extend.

A cold feed extruder, preferable a pin extruder, can be placed in front of the calendar to produce a strip which is fed to the calender via a conveyer belt. Extruders with a diameter from 50 to 250 m m are used depending on the capacity needed. See table below.

Typical capacity of a pin extruder for feeding calendars:

<table>
<thead>
<tr>
<th>Screw diameter</th>
<th>60</th>
<th>90</th>
<th>120</th>
<th>150</th>
<th>250</th>
</tr>
</thead>
<tbody>
<tr>
<td>Screw length, L:D ratio</td>
<td>10</td>
<td>12</td>
<td>14</td>
<td>16</td>
<td>20</td>
</tr>
<tr>
<td>Max output, kg/hr</td>
<td>100-250</td>
<td>300-600</td>
<td>700-1300</td>
<td>1200-2000</td>
<td>3500-6000</td>
</tr>
</tbody>
</table>

Let-off and wind-up units

Calendered sheet material has to be taken up in some type of a wrapping cloth which can be a fabric or a holland cloth. To handle that and to wind up the
calendered sheet let-off and wind-up stations for both liner fabrics and sheeted rubber are needed. Cooled rolls for cooling the sheet are also needed.

For the rubber coating of fabrics in large volumes, when manufacturing tyres, hose and conveyor belts, an extensive production line is needed both before and after the calender. With such a production both sides of the fabric has to be rubber coated. The most efficient process is achieved using a 4-roll calender, where both sides are coated at the same time.

The set up of a line for the coating of cord fabric may look like the one in the picture below. Before the calender in the line there are among other things a let off station for the impregnated fabric, tensioning equipment to give the fabric the correct stretch and magazines (accumulator) holding so much fabric that it gives time for splicing the cord without interrupting the production.

On the other side of the calender there are cooling rolls and another tensioning unit and finally a wind-up station for the coated fabric.

A part of a calender production line for coating of fabrics

Calender production (Photo Berstorff)

Thickness control

Modern calender lines are generally equipped with beta gauges instrumentation working on the principle of transmission or reflection. Two or more fixed measuring heads are often installed, but even one movable head, moving crosswise to the production direction is used.
4.3.3 Sheet preparation

Sheets can be made in the thickness of 0.1 to maximum 2 to 3 mm. By increasing the thickness more than 3 mm there will arise a risk for trapped air giving blisters in the further operation.

The temperature on the rolls varies very much with the type of compounds used, but is normally in the range 80 – 100 °C with the bottom roll at a lower temperature. If the temperature for a certain compound is too low the surface will be uneven, the tendency to shrinkage will be high and the close tolerances cannot be kept.

A typical temperature on a 3 rolls calender is:

- **Upper roll** 100 °C
- **Middle roll** 80 °C
- **Bottom roll** 40 °C

The temperature has however been tested for each formula used for the compounds. The surface temperature on the rolls may under normal conditions be controlled within ± 2 °C.

The cooling of the sheet will influence on the calender shrinkage and it is preferable to have a quick cooling. It is also affecting the calender grain which is giving different properties of the material in the calender direction and in the perpendicular direction.

After cooling, the sheet is winded up on a cylinder in a liner or directly on the cylinder after powdering with i.e. **zinc stearate** to avoid that it is tacked together.
4.3.4 Rubber coating

A great part of calendering operations concern coating of fabrics. The dominating example is coating of cord fabrics for different types of tyres, but many other rubber products like hose, conveyor belt, V-belts, reinforced sheeting and shoes are built up with the use of coated fabrics too.

In principle two different techniques are used.

- Frictioning
- Coating

When frictioning, the rubber is forced into the fabric and the operation is mostly carried out in a 3-rolls calender.

Frictioning has more and more been replaced with coating as synthetic fibres in the form of cord replaced natural textiles like cotton and the bonding systems between textile and rubber has improved.

The frictioning effect is reached by having different rotation speed on the rolls. The middle roll which is carrying the rubber runs faster than the bottom roll carrying the fabric. It is important that the rubber sticks to the middle roll and that effect is achieved by selecting a formula giving a very soft compound, normally with high polymer content.

The temperature on the rolls differs from what was said to be the common temperatures in chapter D. The upper roll is usually about 100 °C and the middle roll a little bit lower as the rubber bank will stay there for some time. The bottom roll ought to be rather high up to 125 - 130 °C, which increases the plasticity of the rubber and make it easier to force the rubber into the fabric.

Coating of fabrics is preferable done in a 4-roll Z-type of calender, as it is then possible to coat both side in one operation.

A 3-roll calender is mostly used if only one side needs to be coated, as it is for many industrial rubber products.

The fabric is very often a cord fabric, which is typical for tyres, but woven fabrics are coated with rubber.

Whatever type of fabric and type of fibre is used, it has to be impregnated before coating to give acceptable bonding to the rubber by curing.

The thickness of the coating can be from some tenths of a mm up to a couple of mm, depending on the product it is intended for.

The setting of the bottom roll nip must be done very careful with respect to thickness of the fabric as well of the coating.

By doing so, the rubber compound is pressed between the cords in the fabric and surrounding each cord. In order to achieve an even coating and the right pressure for good adhesion, the roll setting has to be compensated using the special equipment available for this such as cross axis, roll camber and roll bending. The
thickness is automatic controlled by thickness control instruments as mentioned when talking about peripheral equipment above.

The steel cord used in radial ply constructions is coated with rubber in a special calender line where the wires are taken from spools set up in a creel room where around 1 000 spools of cord are mounted in the creel.

The creel room has a controlled low humidity and elevated temperature to avoid the risk of condensation causing corrosion and adhesion problems.

For larger tyres, such as forestry tyres with steel reinforcement, in some cases woven cord fabric with steel cord warps and coated in a conventional fabric calender is used.

4.3.5 Maintenance

A calender line is a complicated and demanding set of heavy equipment being powered by a number of direct current motors, having several gearboxes and a number of bearings of different sizes and is equipped with hydraulic systems.

The line requires preventive maintenance, regular lubrication and check-ups of oil levels. To be sure that all bearings are in good condition check-ups with vibration measurements are done.

For checking the electrical equipment a thermograph is used to find spots which show an elevated temperature, indicating a bad contact or some other problem which must be taken care of. The technique is used for regular check-ups of transformers, electrical boxes, high voltage switches, electrical cabinets, etc in all types of machinery in the factory.

4.3.6 References

- Rubber Products Manufacotring Technology (Bhowmick, Hall, Benarey)
- Technology-Materials-Principles (White, James L)
- Rubber processing and production organization (Freakley, Philip K)
- Rubber (Läroverket AB)

4.4 Spreading

Coating of fabrics by calendering is described in the text about calendering above, but in addition to that method, fabrics can even be coated with rubber by a spreading technique.

In the spreading process, the rubber compound is dissolved in a suitable solvent to achieve the form of dough.

When calendering the total thickness of the coating is normally made in one pass in the machine but by spreading it is common to build up the total thickness by several passes and drying, evaporation of the solvent- between each pass.

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Spreading is one of the first techniques used in rubber product manufacturing as the Englishman MacIntosh already before the invention of curing made raincoats by solving natural rubber in naphtha from stone coal and spread it on a cotton fabric.

Spreading is still an important technique mostly used for high quality products as protective clothing for chemical industry, fire brigades and military purpose, coated fabrics for production of inflatable products and sheets for offset printing.

Typical for fabrics used for these products is coating with many thin layers for absolute tightness (free of pinholes) as well as different polymers used in the different layers.

Protective suits made from spread coated fabric
Photo, Trelleborg Industri AB

4.4.1 Solvents

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

The solvents used may be divided into following groups:

- Aliphatic hydrocarbons e.g. heptanes
- Aromatic hydrocarbons e.g. toluene
- Polar solvents e.g. esters, i.e. ethyl acetate or ketones e.g. methyl ethyl ketone

Chlorinated solvents have to be avoided due to health and environmental reasons.
The following combinations of rubber types and solvent are often used:

<table>
<thead>
<tr>
<th>Rubber type</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>General purpose rubber (NR, IR, SBR, BR)</td>
<td>Heptanes</td>
</tr>
<tr>
<td>Butyl rubber</td>
<td>Heptanes</td>
</tr>
<tr>
<td>Ethylene propylene rubber</td>
<td>Toluene/heptanes 60/40</td>
</tr>
<tr>
<td>Chloroprene rubber</td>
<td>Toluene/ethyl acetate 15/85</td>
</tr>
<tr>
<td>Nitrile rubber</td>
<td>Methyl ethyl ketone (MEK)</td>
</tr>
<tr>
<td>Silicone rubber</td>
<td>Toluene or MEK</td>
</tr>
<tr>
<td>Fluorocarbon rubber</td>
<td>MEK</td>
</tr>
</tbody>
</table>

4.4.2 Solution of rubber compound

The solution process is made in a solution mixer (kneader) which contains of a chamber in which two Z-shaped rotors turn at a friction ratio from 1:1, 5 to 1:2.0. The chamber is double walled to permit cooling to take care of the friction heat, and it is kept closed by a movable lid. The machine can be tilted to make it easier to take out the ready solution.
The rubber compound can be treated in different ways to make the solution process faster:

1. Cut into smaller pieces, placed in a box with solvent and soaks for some hours.
2. Granulated before transferred to the kneader.
3. Heated on a mill before transferred to the kneader cut into thin sheet.

The solvent is then added to the rubber in small portions to avoid formation of unsolved lumps that can be difficult to get rid of. The blades in the kneader are rotating all the time and the process is continuing until the dough has an even consistency. To reach the correct consistency of the dough it may take anything between a couple of hours and a couple of days depending on the rubber compound formula.

Before the dough is taken to the spreading machine the solid content and the viscosity are tested.

### 4.4.3 Spreading machine

The spreading machine is rather simple in its design as shown in the figure below.

*A spreading machine*

The main parts are:

- let-off roll
- spreading part with a doctor knife
- drying zone with steam heated plates
- take up roll

The drive of the machine is connected to the roll under the knife which is connected with a clutch to the back roller and by a belt to the take up roll.
Different types of the doctor knife are used depending on the type of coating to be done:

- Flat or square section
- Tapered section
- V-shaped
- Bull-nosed

The tapered or V-shaped knives are for example used for light coating with good penetration and the bull-nosed for thicker coating. The knife can be positioned in different angles towards the roll, the angle and the clearance between the knife and the roll controls the coating thickness and the penetration into the fabric.

In the drying zone the temperature is gradually increasing from the entry to the exit point. For faster evaporation of the solvent newer machines are using jet-types ovens where hot air is blown over the surface, thereby increasing both the maximum thickness of each pass as well as the speed.

The exhaust from the drying zone is for reason of pollution control coupled to recovery equipment or a filter. Recovering is of course the most economical method as most solvents are rather expensive, but it can be difficult to recover the solvent in processes where a huge mixture of different solvents is used. In these cases some kind of absorption filters are installed for environmental reasons.

For safety reasons the ventilation must be very good, keeping the solvent concentrations below the explosion limit. All electrical installations must be flameproof and all drives, rolls knives etc. must be grounded and good fire fighting equipment must be easy available.

### 4.4.4 Spreading process

The textile is treated for adhesion as described in the text about Textile treatment or alternatively isocyanate is added to the dough used for the first layer of rubber. That method is used if the increased stiffness by dipping in RFL is not acceptable or if the fabric will be coated only on one side and the other side should have the colour of the fabric.

The fabric is fed over the driven roller under the knife. The rubber in form of the dough is placed in front of the knife with a ladle. When the machine starts, the moving fabric and the obstacle from the knife gives the dough a rotary movement in the direction of breadth of the machine. The fabric will obtain a coating of the dough and the thickness of the coating is determined by the position of the knife.

The amount of dry rubber per pass is between 10 and 40 g/m².

### 4.4.5 References

- Rubber Products Manufacturing Technology (Bhowmick, Hall, Benarey)
4.5 Extrusion

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

Extruders are used for shaping ready products or parts to be used in a later operation like inner tube for hoses, blanks for feeding of moulds, parts for tyre building and tyre inner tubes. Ready products like sealing profiles for cars and buildings, tubing etc. can be finished by curing either continuously or discontinuously.

4.5.1 Machinery

Basic layout of an extruder

Cold feed extruder (Photo Colmec)
The design of an extruder is shown in the sketch and consists of the following parts:

1. A barrel of varying size
2. The screw, which pumps the material towards the die
3. In the barrel, some extruders have a vacuum zone
4. Extruder head containing the die
5. A feed cylinder, which helps to feed the material evenly into the extruder
6. A gearbox
7. A drive motor

The size of extruders is given as the diameter of the screw. The number of screw diameters that can be placed along the screw, called the L/D ratio, determines the length of the screw and is a major factor in selection of extruder to match a certain process.

There are two main types of extruders, hot feed and cold feed. As the names imply, in one case the machine is fed with heated rubber compound from an open mill and in the other case with an uncured rubber slab or strip of ambient temperature.

The hot feed extruders represent the oldest technology and are not used to any great extent today. These extruders have short screws with L/D ratios between 4 and 8. The cold feed extruders representing the technology used today are considerably longer with a L/D ratio of 16 - 24.

The longer screw ensures that the rubber material is sufficiently worked and heated before it reaches the die. To make it possible to regulate the temperature in the extruder, the wall of the barrel and the screw are equipped with channels in which water circulates for heating or cooling.

The wall of the barrel is divided into several sections and the temperature can be carefully controlled in each of the sections as well as in the screw.

In certain processes, air and even moisture that can occur in the rubber material must be ventilated or bled off. The extruder is then equipped with a vacuum zone (vented extruder) where the barrel has an extraction port with a vacuum pump applying a vacuum pressure. The screw has before the vacuum port worked the compound to a homogeneous state and to a temperature that permits gasification of moisture and other volatiles.

In order to increase the output from the extruder and to improve the quality of the extruded goods, several different types of screws have been developed. A common way is to change the pitch of the screw and with that the quantity of material which can be pumped through the extruder can vary accordingly. The screws are usually referred to as high or low capacity screws. So called mixing screws are one of these effective screw types.

A popular type of effective screws is pin extruders, which have a barrel in which adjustable pins are mounted. The screw has milled grooves to allow it to rotate
even though the pins are inserted. The pins interrupt the otherwise even flow and thus provide an increased working of the material.

The extruder head is placed in the barrel at the outflow end and is a separate part which can be replaced by different types of heads. In the extruder head the die and the guide tubes (mandrels) which is needed to shape the product are mounted.

Special types of extruder heads are used for extrusion of products with great width, i.e. tyre treads as well for covering reinforced hoses or cables with rubber. In the last case a so called angle extrusion head is used, where the material to be covered with rubber is guided into a case in the extrusion head at a special angle towards the screw i.e. 90° and in that way being covered with rubber.

When extruding large profiles containing several different materials, again like treads for car tyres, two or more pin extruders are often combined together in a manufacturing line. In such a line the different materials from each extruder are joined in the die at the end of the line to accomplish the final profile.

That technique called Dual extrusion is also used by manufacturing i.e. profiles with two different materials i.e. one black and one white compound or a cellular rubber combined with a solid rubber.
The drive motor on modern extruders is of the direct current type or powered by alternating current with frequency changing, which both provide a simple method of adjusting the speed of the screw.

When requirements with narrow tolerances and high precision on measurements have to be taken into account, a laser measuring gauge is a good aid for measuring the profile directly as it emerges from the die. The measurements are calculated in the control computer and are linked back to the driving unit, which regulates the speed to achieve correct dimension.

As the extruded part is further transported on a conveyer belt the dimension regulation can even be obtained by controlling the speed of that belt.

4.5.2 Die manufacturing

The dies can vary greatly in design depending on the cross-sectional shape of the product. The simplest die is the one which is used for the manufacture of a rubber string, consisting of simply a hole, drilled in a steel plate or a tube when it beside the die also needs a guide tube to make the hole in the tube.

Consideration must still be taken to the need of the surface of the product to be made smooth by beveling and polishing the edges of the round hole.

In the manufacturing of strips with more complex cross-sections the requirements on the manufacture of the die are much greater.

When making a die for a complex profile, co-operation between design engineers from both the customer and manufacturer and a compounder is needed in order to obtain a product with the best compromise between product and processing properties.
The manufacturer’s design engineer can with the aid of advanced computer technology, CAD, make a drawing and a design specification for the new profile.

This document is then used in computer controlled tool manufacturing (CAM) which in the first stage is carried out in a spark erosion machine. The job is finished by grinding, polishing and adding mandrels and braces. The grinding is performed with the purpose of making the die thinner and more bevelled in order to facilitate the flow of the rubber compound through the die.

In other sections of the die, braces can be added in order to reduce the flow of the rubber compound in the thicker sections of the profile. The final finishing work is carried out in conjunction with the manufacturing of a prototype die.

It is difficult to theoretically calculate what the final die will look like. The work of developing a new product is therefore based on the practical experience of the designer and toolmaker.

*Die design, utilising CAD (Photo Trelleborg Building Systems)*
4.5.3 Techniques

The quality of the extruded goods, especially the smoothness of the surface and closed tolerances are beside the extrusion technology very much depending on the rubber compound, which in the case of making a finished product in the process has to be formulated for good extrusion properties. As an example influences the viscosity of the polymer, the filling degree and the type of filler heavily on the extrusion properties.

**Die swell** is a function of both design and rubber rheology and may cause the effect that the cross-section of the extrudate will have a bigger area than the hole in the die.

The die can be designed to decrease the die swell i.e. by making long dies which will release the stress in the rubber before the extrudate is leaving the die.

Typical differences between the shape of the die and the extruded section are shown in the figure below.

![Diagram showing typical differences between the shape of the die and the extruded section.](image)

Regarding the influence of the compound all ingredients beside the polymer is decreasing the die swell. EPDM compounds e.g. often contains high amount of filler and oil, and is therefore showing low die swell. The die swell may be tested in a so called **Garvey Die test**.

Temperature control is an important part of reaching good quality and high output from an extruder. The material has to be heated up to get the needed plasticity without coming into the risk zone for **scorching**.

After heating the barrel at the start up of an extrusion process, it is normal that only cooling is needed for both barrel and screw as the generated heat is enough to keep the wanted temperature. As a general role the temperature should successively increase from the feeding point to the extrusion head.
The output from an extruder can be theoretical calculated from data about the geometry of the screw, the screw speed, the pressure in the die and the compounds flow behaviour.

With a well designed screw operated at perfect temperature the output measured in kg/hour is proportional to the screw speed.

4.5.4 References

- Rubber Products Manufacturing Technology (Bhowmick, Hall, Benarey)
- Rubber processing and production organization (Freakley, Philip K)
- Rubber (Läroverket AB)

4.6 Mould curing

Moulding is preferable for volume production of products with closed dimensional tolerances. Sealing rings and bellows etc are typical examples of such products. Tyres may however be considered as a moulding product too. Moulding and curing are carried out in the same process. The moulding is done when the rubber fills the cavities of the mould, while the curing is done subsequently by heating the rubber in the mould.
Fundamental principles of mould curing are connected with the sequential shaping and curing of a rubber compound.

The moulding operation must take into consideration all aspects of the interaction between the requirements for viscous flow and cross linking and the dependence of both of these on temperature.

As usual, technical and economic factors also have to be considered together. The choice of, or the design of a moulding process is then always a compromise imposed by the need to complete the shaping step prior to the onset of cross linking and finally to achieve a reasonable uniform state of cure.

High-volume production will most often justify more sophisticated techniques, while low-volume production will dictate that the expenditure on moulds and moulding equipment should have to be minimal.

To fulfil these requirements three main moulding techniques have been developed:

1. Compression moulding
2. Transfer moulding
3. Injection moulding

All these techniques come in many variations to suit individual requirements of complex shapes, dimensional accuracy etc.

The capital cost of machines and moulds increases from a minimum for compression moulding, through transfer moulding to a maximum for injection moulding.

4.6.1 Machinery

Presses

For mould curing, hydraulically or mechanically operated presses are used to keep the moulds closed. The press consists of a robust frame and one or several press plates which can be pressed together.

The mould is placed between two of these plates, which are heated, and thus the mould itself is heated as well. The heating is carried out using electrical heating elements which act directly or by steam, water or oil being heated separately and circulating through channels in the press plates. The heating of moulds in the rubber industry is not as meticulously and accurately carried out as in the plastics industry.

Moulds

The moulds are made of steel where cavities and any necessary channels are machined with the aid of machining tools. Specialised companies produce the
moulds. Certain rubber factories also have their own mould manufacturing departments while most of them only maintain and repair their moulds.

**Mould maintenance**

Every time a mould has been used in a long production run, or at any time when it is needed during a production process, the mould has to be cleaned in the cavities and at the parting lines to remove the dirt that may have occurred during the production.

Several cleaning methods are available of which most are used when the mould has been dismounted from the press i.e.:

- Washing in a warm alkaline liquid.
- Ultrasonic washing in a warm alkaline liquid.
- Wet blasting with sand or glass.
- Dry blasting with plastic granules or coconut shell.
- Blasting with ice.
- Cleaning with laser.

To receive a perfect result with method 1 to 4 the mould has to be taken out from the press and disassembled. After cleaning, the mould is mounted in the press again and all safety devices are checked simultaneously. If the mould is out of operation for some time, a rust protection treatment has to be applied. If it is to be stored only for a short time, it may be enough to treat the mould with a mould release agent giving some rust protection but still not requiring a removal prior to the use of the mould in the production again. When a specialized rust protection agent is used, the mould has to be carefully cleaned before returning it to the production. The reason is that the agent is going into parting lines and is exuded when the mould is heated.

The methods 5 and 6 can be used for hot moulds mounted in the press.

The reasons for mould fouling can be found with the compound, in the steel used for the mould manufacture or the processing variables. It can be worthwhile to use a processing aid agent in the compound to reduce the fouling.

### 4.6.2 Techniques

**Manufacturing methods**

The moulding processes can be categorised into three main groups as mentioned earlier:

- Compression moulding
- Transfer moulding
- Injection moulding
The first method mentioned above is the oldest and simplest method. Development has since been moving towards transfer moulding and above all towards injection moulding with the thermoplastic industry being the primary leader in this field.

**Compression moulding**

In compression moulding, the rubber compound is formed into a blank, which is then placed in the mould cavity. In order to ensure that the mould is filled properly, a certain excess charge of between 5 - 10 % is required.

A simple punching or cutting procedure directly from the rubber slabs produces blanks or alternatively the rubber compound is squeezed into shape with the aid of a plunger or screw through an extruder die. The strip obtained is then cut into suitable lengths.

The supply of heat depends on the rate of heat conduction from the mould to the rubber. Since the heat conductivity of rubber is poor, heating is slow and the curing time is therefore relatively long.

Typical curing times are from 3 minutes for thin goods to several hours for products with thick walls. In the latter case, it is more efficient to pre-heat the rubber. This can take place in a hot air oven or in a microwave oven up to temperatures of approximately 100 °C. When heated over 100 °C the risk of scorching becomes excessive.
The advantages of compression moulding are primarily the following:

1. The method is simple and only requires relatively simple presses and moulds. It is an appropriate method for short runs.

2. Allows manufacturing of composite products which contain non-rubber reinforcing material (laminates).

3. Suitable for products with large surface or large spreading.

4. Can be used for rubber compounds with high viscosity and poor flow properties.

The disadvantages of compression moulding are the following:

1. The preparation of blanks and the insertion of blanks into the mould are time consuming.

2. Complicated cavities can be difficult to fill out completely.

3. The formation of flash is extensive and the variations of the hot mould cavity dependant dimensions are relatively extensive.

4. The production rate is relatively low.

Transfer moulding

Transfer moulding is a natural progression in the development when attempting to limit the disadvantages of compression moulding. The blank is loaded into a loading chamber and is then distributed into several cavities. The rubber is squeezed out of the loading chamber by means of the closing mechanism of the press itself, or with separate pistons, into each respective cavity.
Since the rubber is forced to flow through channels and gates, preheating takes place in the rubber. This preheating significantly reduces the curing time. Provided that the injection pressure does not exceed the closing pressure of the mould, a well balanced dosage of rubber into each cavity will be obtained and the formation of flash will be reduced to a minimum.

The advantages of transfer moulding are primarily the following:

1. The preparation of blanks and their handling is made considerably easier.
2. The preheating of the rubber reduces the curing time.
3. Since the rubber is preheated it flows easier and fills the mould cavities more efficiently.
4. The mould is closed when the rubber is injected into the cavities, which means that less flash is formed and smaller dimensional variations of the product are obtained.
5. For rubber-metal bonding, the rubber makes better contact with the metal in the form of a new and “fresh”, clean surface.

The disadvantages of transfer moulding are primarily the following:

1. The moulds are more complicated and more expensive.
2. Parts with textile inserts cannot be produced.
3. The method requires materials that are relatively simple to process.

Injection moulding

[Diagram of injection moulding]
During injection moulding, the press unit and the injection unit are two separate units with separate operating controls. The press unit can have the mould placed horizontally or vertically. The injection unit can have a combined plasticizing and feeding screw or alternatively the screw is only intended for the purpose of plasticizing and the injection itself is carried out using an attached plunger unit. The positioning of the injection device varies between different makes of machines.

It is an advantage if the feed opening for the rubber strip is placed at comfortable working height. One extruder unit can sometimes serve several presses by moving in a pre-programmed pattern. By means of a high injection moulding pressure, a short injection time and a considerable amount of preheating of the rubber is obtained. The preheating can achieve the same or higher temperatures than those of the mould and the curing time then becomes extremely short.

A special variety of injection moulding is the use of gear pumps as an injection unit. The injection process then becomes slower but the quantity of rubber per shot is almost unlimited.
The advantages of injection moulding are primarily the following:

1. The handling of blanks is completely eliminated.
2. The mould is filled in a closed position and the formation of flash can in certain cases be completely avoided.
3. Complex cavities and flow channels can be filled easily.
4. The curing time is very short.
5. The process can be easily automated.

The disadvantages of injection moulding are the following:

1. The moulds and machines are considerably more expensive.
2. If an injection unit serves several moulds, the material in the common injection unit is limited to one particular type of compound.
3. The process requires greater technical know-how.
4. There are strong requirements for the rubber compound to have low viscosity and to be homogenous.
5. Gates and injection runners contain vulcanised rubber, which must be discarded.
6. Laminated parts cannot be produced.

4.6.3 Processing problems

Moulding processing of rubber products can be disturbed for many reasons. In the past, the rubber industry hired special faultfinders, so called “trouble shooters”, in order to find and correct mistakes or faults. Nowadays, the causes of most faults can be prevented or eliminated, but this requires that all personnel involved in the process have the proper knowledge and training, and that they follow the instructions given.

The following section describes various types of faults and how they can be dealt with.

- Shrinkage
- Mould flash
- Porosity
- Flow marks
- Back-rinding
- Set-up efficiency
Shrinkage

The thermal linear expansion of rubber is approximately 10 - 20 times larger than that of metal. This means that a mould cured rubber product will shrink approximately 2 % when cooled.

The mould cavity must thus be made so much larger so that this shrinkage is compensated for. The amount of shrinkage can be calculated reasonably accurately if the polymers of the rubber material and the plasticiser contents are known as well as the curing temperature of the rubber is to be cured.

The shrinkage can vary somewhat in different directions due to the fact that rubber molecules are orientated in the direction of flow. Both experiment and experience are used as guidelines in designing new moulds.

Mould flash

Flash at the mould parting lines are due to the mould being over-filled or that the rubber, due to thermal expansion, increases in volume. Countermeasures would be to use “tightly sealed” moulds, to preheat the rubber in order to avoid thermal expansion and to arrange flash grooves along the parting lines of the mould halves.

Porosity

Many factors can cause blisters and porosity. Trapped gases or air trapped in the mould cavity can cause blisters. The most common cause of the formation of porosity in the bulk of the product is simply that the vulcanisation process has not been effective, i.e. the material is under-cured. If the curing is terminated before the centre of the part has reached a certain curing state, porosity will occur when opening the mould. The curing state when porosity will not occur is called "the blow point".

Flow marks

Marks or blemishes on the surface of the product are often caused by some variety of fault in the flow process. First of all, however, an investigation should be carried to ensure that it is not a defect in the mould surface itself which is the cause. A contributing factor to flow marks could be the early stages of scorching. Flow marks can often be dealt with by changing the direction of the flow through some slight change in the composition of the material, mould or machine setting.

Back-rinding

This disturbance manifests itself as a sore in the product at the parting line of the mould and as “holes” at the gates. The reason is that the thermal expansion of the rubber occurs at the same time as the surface starts to cure. The most effective way to deal with this processing problem is to prepare the rubber with high preheating temperatures so that thermal expansion is reduced or completely eliminated.

Set-up efficiency

The setting-up time of moulds is the time between the last piece cured in one operation series and the first piece produced in the next series. It is important to prepare as much as possible for such a change to minimise all the actions which
have to be taken when the press has been stopped (down time set-up) by eliminating operations which can be performed while the press is still in operation, i.e. set-up in production.

If the following steps are carried out as set-up in production it can reduce the time for the down time set-up from hours to less than 10 minutes:

- Preheating the mould to curing temperature.
- All mounting devices to be prepared.
- All fittings controlled to be correct.

The down time set-up will be facilitated by using:

- Quick fastening tools.
- Rulers to fix the mould.
- Co-operation by several operators.
- Good helping devices i.e. for lifting.

A good way to study the job is to make a video of the procedure and analyse the film.

4.6.4 Post-processing

Postcuring

When moulded products are demoulded they cool down slowly and a certain amount of postcuring must be taken into account. A rule of thumb is that vulcanisation takes place up to approximately 90 % of the optimal level in the mould and the remaining 10 % of curing is achieved during the cooling period.

In certain cases, this percentage can be lowered if you maintain or add heat in a postcure oven.

Such ovens are also useful in achieving an extra high degree of vulcanisation. This is important for seals, for example, which require a low compression set. A typical postcuring process could take 15 minutes at 150 °C provided that the product is warm from the start.
It is economically sound business practise to replace expensive curing time in the mould with the cheaper process in the oven. Furthermore, a certain unevenness from the vulcanisation in the mould can be compensated for in the postcure.

Certain special purpose rubbers require postcuring for several hours and even up to 24 hours.

**Maintenance**

To secure an optimal result at postcuring in a conveyor oven a regular maintenance with changing of filters, control of curtains, checking the airflow and control of the temperature has to be performed.

In the postcuring process plasticisers evaporate from the rubber and condense on the walls of the oven and in its ventilation channels. This presents a risk of fire, and to eliminate that risk a regular cleaning has to be done. How often the cleaning should take place depends on the time of use and the degree of condensation. The same rules apply also for post curing chambers.

**Deflashing**

Nearly all moulded products have flash along the mould parting lines. The following methods are used in order to remove the flash.

1. **Trimming with the aid of flash ridges** - In the mould there are flash grooves in the parting plane. These grooves are filled with rubber, which can then be torn off since the flash is made to become very thin in the transition zone between the product and the groove.

2. Cutting with a hot knife - Rubber is easier to cut and tear in a warm state. This property is utilised when trimming with warm knife, which is heated in a device similar to a soldering iron.
3. **Punching** - Flash can also be removed using an automatically or manually operated cutting die.

4. **Freezing** - If rubber is cooled down to a low temperature below its brittle point it becomes breakable. Using liquid nitrogen to quickly freeze the flash can take advantages of this property in order to remove flash. Since the flash is thin it becomes brittle first and can easily be broken off by tumbling the articles in a revolving drum.

**Surface finishing**

In order to modify the surface of the rubber to reduce the friction or improve the adhesion, different kinds of surface finishing processes are used such as chlorination or radiation with UV light.

**Assembly**

A rubber product can consist of several parts, which are fitted together. An example of this is a safety mask. In addition to the frame, the inner mask and air vents which are made of rubber, there are also a large number of plastic parts included. They are all assembled into a functioning product.

**4.6.5 Moulds**

**Design**

The desired dimensions of a product are determined in a three-dimensional model in digital form by utilising the computer programme CAD, which stands for Computer Aided Design. From this model the mould, which will give the product its final appearance is designed. The design of the mould presumes that the type of machine and the material have been decided upon and that the necessary data for these are known. A useful aid in this context are so called mould filling programmes which conduct computerised simulations of how the material flows and fills the cavity.

Using this type of tool already in the design stage can prevent certain types of processing problems and provide guidelines for determining the sizes of channels, and the positioning of gates and working out the possible number of cavities.

An important factor is the shrinkage of the material. It normally amounts to approximately 2 % and must be added to all measurements in the cavity. The shrinkage is primarily dependent on the temperature and occurs in all the three dimensions, but in practice shrinkage can vary in different directions depending on the orientation of the rubber molecules.
Manufacturing

Steel is the most common material used to produce moulds. Special corrosion resistant types of steel are used. After machining, the material is tempered in order to increase the hardness and improve the wear resistance. The machining is carried out with machining tools which perform various operations such as turning, milling, drilling and electro-erosion. These machining tools are controlled by computers, which can be digitally programmed from the computerized drawing. (CAM = Computer Aided Machining).

Electro-erosion is a method whereby an electric arc between an electrode and the mould surface slowly removes the metal. Uneven surfaces and surfaces with curvatures in several planes can be formed with great precision. Another advantage is that all surfaces are given the same degree of evenness. It is common practice to produce smaller test moulds first. These can be used in order to produce a pilot run of a small quantity of products.

The final mould can then be produced with a high degree of certainty concerning its dimensions and operation. Sometimes it is possible to incorporate the test mould as an integrated part of the final mould.

The cavity is the void in the mould to be filled with rubber in order to obtain a product of specified size and appearance.

Maintenance

The maintenance is mostly performed to preserve the proper operation of moving parts, check the operation of and overhaul of the heating elements and repairing any damages which may produce unwanted marks on the moulded part.
Surface treatment of the cavity is carried out when the rubber material has a tendency to stick to or soil the metal surface. This treatment varies from regular spraying of mould release agent to more permanent surface treating using metal or polymer alloys.

4.7 Rubber-metal bonding

In many cases, it is desirable to apply rubber to metal. For example, when rubber is used for corrosion or wear protecting linings or for the covering of rolls.

In many engineering parts such as dampers, couplings, solid rubber wheels or sealing rings, rubber is combined with metal.

For example, the metal can have the task of making the design more rigid, facilitating the installation of machine parts or taking up a load. The best result is obtained when the rubber is moulded, vulcanised and bonded to the metal in one operation.
4.7.1 Bond system characteristics

The method of bonding rubber to metal with a bonding agent dissolved in a solvent is the most common method used today. In order to avoid environmental problems in the handling of solvents, water-based bonding agents are available.

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

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

The adhesive contain halogenated polymers, carbon black plus other fillers and special cross-linkers that are compatible with the primer, as well as with the rubber to be bonded. Di-and poly-functional chemicals that are capable of reacting across the interfaces between the adhesive and the rubber and the adhesive and the primer to form stable bonds.

A definitive description, which comprehensively summarises bonding agents, does not exist. Their compositions are well kept secrets of the manufacturers and they are only alluded to in the patent literature.
Sometimes one bonding agent is sufficient, in other cases two of them must be used. The one closest to the metal is normally called the primer and the other the bonding agent. For different types of rubber, different metals and even different manufacturing procedures various adhesion systems are recommended. Recent development has moved in the direction of making the adhesion systems more versatile. With a few bonding agents or systems, most practical applications can be catered for today. Some of the most common trademarks are e.g. Chemlok, Chemosil, Megum, Thixon and Ty-Ply.

The rubber to metal bonding reactions are very complex as there are several reactions taking place simultaneously. These reactions must be finalised during a short period of time while all layers an interphases still are reactive, in order to obtain a durable bond.

The different reactions that are taking place are shown in the Figure.

_Schematic of vulcanisation bonding process_

All the chemical reactions, in each of the three organic layer, that form a rubber to metal bond (primer, adhesive and rubber) must take place during the moulding step.

The crosslinking reactions are obtained by either a heat reactive resin or an externally added crosslinker which increases the molecular weight and cohesive strength of each layer.

Simultaneously each layer undergoes reactions with the layers immediately below and above it. These reactions are caused by the same chemicals that allow for the internal crosslinking to occur.

The “first link” in a rubber to metal joint is the primer to metal interface. The organic resin in the primer reacts with metal oxides on the surface of the metal to form strong and durable bonds. Such bonds are typically a mixture of physical adsorption, chemisorption, ionic and covalent bonds which are very resistant to attack from water, heat and chemicals.
The next link in the rubber to metal bond is the one between the primer and adhesive interface. Curatives in the adhesive migrate into the primer during vulcanisation and form chemical bonds between the adhesive and primer. Chemical species in the primer diffuses and knits with the adhesive and further strengthen the bond between the adhesive and the primer, because there is a good compatibility between the two.

There is also a migration of curative from the adhesive into the rubber during the vulcanisation. This curative form chemical bonds between the adhesive and rubber. Bonds which span across the interfaces in an assembly are normally called “cross-bridges” to differentiate from the normal cross-links that occur within the layers themselves.

Sulphur that migrates from the rubber into the adhesive also contributes to form additional cross-bridges between the rubber and the adhesive.

**Cure kinetics of rubber-to-metal bonding agents**

Curemeters were invented back in the late 1950s and early 1960s and have ever since provided the rubber industry and others with valuable information on how the curing reactions of heat-curable rubber compounds are progressing during the vulcanization stage.

Since many rubber-to-metal bonding agents can loosely be described as heat curable polymers, dissolved in suitable solvents, the same principle of curemetering should therefore apply for rubber-to-metal bonding adhesives as for ordinary rubber compounds.

Most, if not all, commercial adhesion systems are proprietary products and their actual compositions are well kept secrets by the manufacturers and therefore not well known by the users. Nevertheless, patent literature and numerous articles written during the last 40 years make it possible, at least in a qualitative sense, to draw some conclusions about the composition of the most frequently used primers and adhesives.

Better knowledge of the bonding agents would vastly increase the possibility of bringing the adhesion systems on a par with the rubber materials regarding the determination of important reaction kinetic, since there are good reasons to believe that the reaction sequences of the materials forming the bond are critical for a strong and durable adhesion.

Dynamic Mechanical Thermal Analysis (DMTA) is a useful analyzing techniques for these purposes. DMTA as a tool in evaluation of important reaction kinetic properties of both the bonding agents and the rubber material.

The basic function of a Dynamic Mechanical Thermal Analyzer (DMTA) is to subject the (polymer) sample to an oscillating strain and measure the mechanical responses. Figure below. The strain is, depending on material and sample geometry, usually set at a very low value. This in turn makes it possible to detect small changes in the mechanical behavior of the material.
Example: The modulus responses obtained from studies of the individual materials (primer, adhesive and rubber) under semi-isothermal conditions are presented in Figures below. In comparison, the primer is very scorchy and fast curing, with a plateau curving curve. A weak tendency for the primer to revert at the highest temperature can be seen in Figures below. The shear modulus increase from the point of cure onset to full cure is about 40 x, which indicates a high crosslink density.

Dynamic Shear modulus in Isothermal condition

![Graph showing shear modulus over time for different materials at 130 °C (Primer, Rubber, Adhesive)]
The figures also show that the adhesive is less scorchy and slower curing than the primer. Furthermore, the adhesive shear modulus has a very pronounced marching modulus behavior. The modulus increase from cure onset to log $G' = 6.5$ (corresponding to 255 min at 150 °C) is 90 x. This cure level is probably never reached in a real process. A more realistic estimate would be that the modulus would increase (say) 10 x, which corresponds to approximately 40 min at 150 °C.
Figures also show that the rubber has a typical sulphur/CBS delayed action cure, which has been further amplified by the addition of Santogard PVI retarder.

The increase in modulus from cure onset to full conversion is 4 x, which is about 10 times lower than for the primer. Due to the typically low crosslink density of the rubber, this is also expected.

The primer has reached a degree of conversion of more than 90 % at the time when the curing reaction of the rubber commences. Simultaneously, the adhesive has started to cure but since the adhesive lacks a definite cure plateau; it is difficult to determine any specific degree of conversion when the rubber has reached the cure onset. An estimate suggests something of the order of 15 – 20 % at 130 and 150 °C.

In order to manufacture highly reliable and durable rubber-to-metal bonded articles, the bonding agents have to be characterized so that reaction sequences of the primer, adhesive and rubber can be matched in the best possible manner.

4.7.2 Adhesion

Adhesion between different types of rubber, rubber compounds and metals

When various rubber materials are bonded to various metals it is normally difficult to predict what the result will be. Small changes in the composition of the rubber compound, the metal alloy composition or the surface structure, and the choice of pre-treatment or bonding agents can have a great and often unexpected influence on the adhesion.

The technique has primarily been developed for steel and aluminium, which are the most common materials used, and which normally, also give the best adhesion. For brass, bronze and other alloys the adhesion varies from good to poor depending on the composition of the alloy.

It should be pointed out that the same technique can be used to bond rubber to a large number of non-metallic materials, e.g. glass fibre reinforced thermoplastics, thermoplastics such as polyamide and ceramics etc.

Good adhesion is obtained with most of the common types of rubber, that is to say NR, SBR, IR, BR, CR and NBR. There are no significant differences in using these rubbers. There is a tendency that polar materials such as CR and NBR, are easier to bond than the rubber materials NR or SBR with little or no polarity in their molecular structures.

Ethylene-propylene rubber and butyl rubber achieve a lower level of adhesion than the types of rubber mentioned above.

Other types of rubber, like the more specialised types of rubber such as fluoro and silicone rubbers are due to their chemical structure and low tack properties more difficult to bond to metal with acceptable results.
Acrylic rubber and urethane rubber have a polar molecular structure, which facilitates adhesion.

In conclusion, most types of rubber can with the use of today's techniques, be bonded to most metals with acceptable results, that is to say they rupture during adhesion testing in the rubber and not in or at the bonded surface.

The limitations in the possibilities of achieving an acceptable bonding are primarily depending on certain manufacturing procedures, e.g. open curing, or the adhering surfaces are subjected to the influence of chemicals.

4.7.3 Manufacturing

The flow chart for manufacturing of moulded rubber-metal parts is shown below. It should be noted that special care must be taken to obtain a clean metal surface with the desired structure. This requires either mechanical (blasting, machine cutting, or wire brushing) or chemical cleaning.
The purpose of the treatment is partly to remove rust, oxide scale, layers of other impurities, and partly to give a rough surface which due to the enlarged surface area and its capabilities of mechanical bonding will provide better adhesion.

For **blasting**, sharp edged particles with a particle size of approximately 0.3 - 0.9 mm are used. Blasting with steel grit should not be used on non-iron metals, since imbedded iron particles can produce galvanic elements with the risk of blister formation and poor adhesion.

**Chemical cleaning** can take place both in acidic and alkaline environments. A large number of commercial products are provided for this purpose, the exact compositions of which are not generally known. The cleaning is often combined with a chemical modification of the surface, e.g. the formations of phosphates, or for certain metals an oxidation process intended to facilitate the adhesion or reduce the risk of corrosion.

The question of whether the mechanical or chemical method is the best depends on the parts that are to be produced. For small and thin metal parts, which cannot withstand blasting, chemical cleaning is the only choice.

Chemical cleaning is often cheaper in long runs of production with small metal parts and has in later years been developed to a greater reliability. Often a combination of chemical and mechanical pre-treatment is used.

**The metals are degreased** before surface treatment and often afterwards as well. This can take place in alkaline baths or with solvents. After the processing, the metals should be well protected from contamination, e.g. from dust, fingerprints or silicone oil in aerosol form, which is a common mould lubricant in the rubber industry. The relative humidity for the storage of clean metal parts should not exceed 50 %.

**The adhesion agents are applied by means of** brushing, roller coating, spraying or dipping depending on the shape of the parts and the size of the production runs. The vaporisation during the spraying can take place with or without compressed air in the spray gun. Electrostatic spraying can minimize the loss of material.

It is often desirable that the application is carried out as quickly as possible, before the purity and adhesive capacity of the metal surface are impaired. Solvents are evaporated in ventilated drying ovens, where also a certain amount of pre-curing of the bonding agents can take place.

The process can be automated for long runs of production and be made to operate continuously. As in the process of gluing, there is an optimal thickness of the layer of bonding agent, which depending on the degree of smoothness of the metal surface is normally between 10 - 20 μm per layer.

The surface treated metal parts must be protected from dust, moisture and contaminants. The surfaces must not be touched by bare hands, since an ordinary fingerprint leaves small amounts of impurities in the form of skin grease and dirt, which can impair the adhesive properties.
Phosphatizing

Phosphates have been used for many years in the rubber bonding industry to promote the adhesion of rubber to metal substrates. Many types of phosphate treatment are used including zinc-modified phosphate, iron-modified phosphate, calcium-modified phosphate, nickel-modified phosphate and manganese phosphate. These phosphates also provide corrosion resistance to the metals on which they are applied.

Background

Phosphates are usually applied using three, five or seven stage systems depending on performance requirements and types of parts being coated. In a five or seven stage system, parts are cleaned to remove the soils present and then undergo rinsing. The parts can then be etched in an acid bath and rinsed prior to applying the phosphate coating or they can go into the phosphate bath after cleaning and rinsing. After coating, the parts are again rinsed and an optional sealer can be applied. After the parts are dried, they undergo an adhesive application. Any one of a variety of rubbers can be bonded to the treated metal using standard established procedures. Table below shows typical phosphate processes for, three, five and seven stage systems prior to rubber bonding.

Typical phosphate process conditions for three, five and seven stage systems:

<table>
<thead>
<tr>
<th>Stage #</th>
<th>Three - Stage</th>
<th>Five - Stage</th>
<th>Seven - Stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Clean/phosphate 54 – 71 °C 2 – 4 %</td>
<td>Alkaline clean 49 - 71 °C 1 – 4 %</td>
<td>Alkaline clean 49 – 71 °C 1 – 4 %</td>
</tr>
<tr>
<td>2</td>
<td>Overflowing rinse</td>
<td>Overflowing rinse</td>
<td>Overflowing rinse</td>
</tr>
<tr>
<td>3</td>
<td>Non-chrome or chrome sealer 30 – 60 seconds</td>
<td>Phosphate 49 – 71 °C pH 3.5 – 5.5 2 – 7 minutes</td>
<td>Acid cleaning 49 – 66 °C 1 – 3 % 60-90 seconds</td>
</tr>
<tr>
<td>4</td>
<td>Overflowing rinse</td>
<td>Overflowing rinse</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Non-chrome or chrome sealer 30 – 60 seconds</td>
<td>Phosphate 49 – 71 °C 1 – 4 % pH 3.5 – 5.5 2 – 7 minutes</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td>Overflowing rinse</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td>Non-chrome or chrome sealer 30 – 60 seconds</td>
</tr>
</tbody>
</table>
**Chemical preparation**

Chemical preparation involves, as already shown, a series of process steps, which should all be optimally geared to their purpose. Moreover, a special process has to be selected for practically each metal, depending on its subsequent use in the field of rubber-to-metal bonding. As a consequence, the suitability of such processes for universal use with large numbers of parts or large throughput is limited, because they are relatively expensive.

Alongside this economic aspect, ecological factors also have to be considered. For example, purification of the waste water produced by phosphatizing accounts for about 50% of the plant cost. The metals that are most commonly used to produce rubber-to-metal parts are steel, galvanized steel and aluminium. In addition, plastic substrates are often used instead of metals.

**Steel**

A thick phosphate layer provides good protection against corrosion. However, it is not suitable for metals that are intended for use in rubber-to-metal bonds. The potentially high tensile and shearing forces in the bonding zone could cause cracks to form in the phosphate layer. In general a microcrystalline zinc/calcium phosphate layer with a thickness of about 1 to 2 μm (this corresponds to about 1 to 2 g/m²) should be applied.

This extreme requirement can only be realized by varying the time, temperature or concentration during the passivation process. In most cases the concentration of the passivation bath is increased so that the usually automatic process does not have to be modified.

During passivation, which is mostly carried out with acidic solutions of trivalent or hexavalent chromium salts, the phosphate forms complexes (reducing the thickness of the phosphate layer) and a protective film forms on the surface of the phosphate crystals. This film increases storage time and improves corrosion resistance.

The following diagram shows the sequence of steps in the phosphatizing process.

![Diagram of phosphatizing process](image)

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Deoxidation is necessary if the metal parts are badly rusted or, if cast steel is to be phosphatized, to remove the so-called metal skin (firmly adhering layer of iron oxide) before further processing is carried out. The metal skin can also be removed by mechanical means (blasting).

A temperature of ≈ 110 ºC should be maintained during drying to ensure that all moisture is expelled. In bonds with elastomers with poor gas permeability (e.g. IIR), residual moisture could cause primers and adhesives to be lifted off the substrate by the steam generated at high vulcanization temperatures.

**Practical phosphate coatings**

Means frequently used to accelerate and refine (the faster the total surface is covered with coating of fine and small crystals) the deposition of a phosphate coating are:

- **agitation of the immersion solution**
- **impinging of a spray bath at high pressure**
- **chemical activation of the metal surface**
  - the number of nuclei formed can be increased by adding oxidizing chemicals to the phosphate bath such as nitrate, nitrite or chlorate
  - the number of nuclei can also be increased by treating the metal surface with an alkaline or neutral solution of titanium or a weak oxalic acid solution
  - vapour degreasing in a chlorinated solvent prior to phosphating usually reduces crystal size probably through iron chloride deposition
  - pickling activates steel surfaces by opening up more active centers
  - copper and other metals more noble than steel can be deposited which will accelerate phosphate deposition by providing more nuclei
  - extremely fine or microcrystalline zinc phosphate crystals can be produced by incorporating into the crystal lattice other metals that will grow in the crystal lattice imperfectly. Metals like Li, Ba, St, Ca and Ni react in this fashion.

The moulding operation, when the rubber is vulcanised to the metal, can be done using the three well-known methods, compression moulding, transfer moulding and injection moulding. Transfer moulding has an advantage over compression moulding in that the hot rubber is transferred into the mould, which reduces the curing time. This also means that fresh newly reworked rubber comes in contact with the bonding surface of the metal substrate.

In compression moulding, great care must be taken to avoid contamination of the metal with dust or mould release agent from other manufacturing operations.

Injection moulding provides short cure cycles, which are however adversely affected by the time needed for the insertion of the metal parts. Many adhesion
systems are not adapted to the high curing temperatures (180 - 220 °C) which are common in injection moulding.

When the rubber flows in the moulds, there is risk that it shears the bonding agent away from the metal surface. In general however, adhesion agents have been developed to resist this effect. A certain amount of pre-curing of the adhesion agent can increase its resistance to unintentional removal. Appropriate mould design, shape of blanks and gate positionings also contribute to reducing the risk. Poor adhesion is obtained if the rubber is allowed to slide over the bonding surface after it has started to cure.

Curing time and curing temperature are often critical factors in obtaining good adhesion largely depending on the different effects they have on the vulcanisation and hardening rate of the rubber and the bonding agents.

**Open curing** of rubber-metal articles is used e.g. in the rubber coating of rolls or in rubber linings for tanks and similar products. Because of the generally diminished pressures in the open vulcanisation process, great care must be taken to avoid the trapping of air during the application of the rubber layers. A high level of tack is desirable in the rubber solutions and rubber layers used.
4.7.5 Levels of adhesion

In principle there are two methods of measuring the adhesive force. In the peeling method (ISO 813), the force required to pull off a rubber strip at an angle of 90° from the metal is measured (normally in kN/m). In the tensile method (ISO 814), the breaking load is measured (normally in MPa) by pulling the rubber perpendicularly from the adhering surface.

As guidelines for assessing adhesion, values tested according to ISO 813 and 814, the figures in the table below can be used. The difficulty in practice, however, is not in obtaining occasional high values but to maintain a guaranteed minimum level during the production process.
It should be noted that some of the values, which are designated as poor in the table, would be designated as acceptable or excellent for glueing operations with vulcanised rubber. This would suggest that the differences in the capacity of the methods would favour the vulcanisation method.

Levels of adhesion value:

<table>
<thead>
<tr>
<th>Values</th>
<th>ISO Peel kN/m</th>
<th>813 test</th>
<th>ISO Tensile MPa</th>
<th>814 test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excellent</td>
<td>&gt;25</td>
<td>&gt;6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Good</td>
<td>15-25</td>
<td>4-6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acceptable</td>
<td>5-15</td>
<td>2-4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poor</td>
<td>&lt;5</td>
<td>&lt;2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The values are only applicable to rubber compounds with good tensile strength. Depending on the design of finished parts, values of a somewhat lower level are often obtained.

As it has previously been made clear, the levels of what is an acceptable adhesion has not been precisely defined and could therefore be said to be ambiguous. As a rule it means that the break generally takes place in the rubber layer itself and not at or in the joining surfaces. For all practical purposes, however, the rubber material is also required to have a satisfactory level of tensile strength and tear strength.

The adhesion can be impaired by several external factors. Among these are:

1. The temperature

The adhesion values decrease relatively marginally at temperatures up to 100 °C for ordinary types of rubber and metals, but starts to decline somewhere within the range of 100 - 150 °C and will be very low or zero at 200 °C. This applies to tests over a short period of time.

For long-term tests, the rubber and adhesion layer age in the normal way, which is why the adhesion values decrease with time. The lower test values, which are obtained at higher temperatures both with and without ageing, can thus be attributed to a weakness in both the rubber material and the adhesive layer.

2. Humidity, water

Under the influence of high humidity and water, diffusion can take place into the adhesive layer and this can result in corrosion of the bond substrate with a subsequent reduction of the adhesive properties.
Traces of chemicals from previous acid treatment operations carried out on the metal or the liberation of hydrochloric acid from insufficiently stabilised bonding agents can greatly accelerate the ageing attack.

3. Oils, fuels, solvents

Provided that the correct types of rubber and bonding agent have been chosen these media do not create any severe problems that cannot be dealt with efficiently.

4. Chemicals

Acidic or alkaline solutions can very quickly destroy the adhesion, especially if the bond is under a mechanical load. Appropriate systems and methods can normally be tried experimentally in order to find a method of prevention, but no general recommendations can be given.

5. Fatigue

For static or dynamic stress, the bond will fail in fatigue. The effect is the same as for normal rubber materials and not a critical phenomenon for normal stress conditions. Certain roll coverings and rubber vibration absorbers are examples of products, where the bond is subjected to considerable fatigue due to dynamic stress.

4.7.6 References

- Preparation methods for rubber-to-metal bonding (Henkel KGaA, Dusseldorf)
- B.A.Sievers e.a., Rubber Div Meeting. ACS, paper No 120 (Cleveland OH, Oct. 16-19, 2001)

4.8 Vulcanisation

4.8.1 Autoclave curing

Curing in an open steam vessel (Photo Trelleborg Industri)
For discontinuous curing, autoclave curing is used. The curing takes place in a vessel (autoclave) where heating is achieved using steam under pressure.

Autoclaves are used for a large variety of purposes e.g. vulcanisation of extrudates, vulcanisation of large products unsuitable for moulding, forming of extrudates (e.g. car radiator hoses) and post vulcanisation of large mouldings and mass produced items like e.g. O-rings

Two types of autoclaves are in common use, unjacketed and jacketed.

In the unjacketed type steam is introduced directly into the autoclave and condensates on the walls of the autoclave and on the items under vulcanisation.

The jacketed autoclave type has a double wall so that the steam may be circulated in the jacket, to provide heating without direct contact with the products. An inert gas can then be introduced in the autoclave to eliminate oxidation and permit brightly coloured articles with good surface finish to be produced. Gases are normally poor conductors of heat and thus increases the curing time.

The temperature with both gas (most often air) and steam methods is normally about 150 °C.

Typical products being cured in steam are hand build and larger extruded articles.

Large, heavy articles like e.g. paper machine rollers require a “stepped cure“ which involves raising the autoclave temperature to the maximum vulcanisation temperature via a series of steps to give a relatively uniform temperature distribution through the product during heating.

Radiator hoses for cars are example of products being fitted on a core and cured in open steam.

Steam curing requires a great deal of manual work from one processing stage to the other, and this contributes to the high cost of autoclave cured products.

Autoclaves are pressure vessels and need to comply with general regulations for pressure vessels, which require regular testing and foolproof interlock mechanisms to prevent the door from open while under pressure. Even very low pressures can exert considerable forces over the door.

4.8.2 Non-pressurized curing

The easiest way of curing would be to simply put the pre-moulded rubber part in a heating chamber. This is however not entirely as simple or as uncomplicated as it first appears to be, since the rubber compound must not contain any moisture or other volatile components which can evaporate when heated and thus cause blisters and porosity.

If air is chosen as the heating medium, it is necessary also to limit the level of the temperature in order to prevent surface oxidation from becoming excessive.
The method has had relatively limited use for the reasons mentioned above, but it is used for instance when curing rubber coated fabrics and products made from such materials like inflatable boats, airbeds and certain types of rubber footwear.

4.8.3 Continuous curing

Continuous curing is particularly suitable for rubber products that are long and with a relatively constant cross section like e.g. rubber profiles, tubes, reinforced hoses, cables and sheeting of different kind.

The curing process is in many cases directly coupled to the forming process i.e. the curing equipment is directly attached to the extruder. This eliminates the need of intermediate handling and storage which means that the formed material, in this case the profile, arrives to the curing machine in a pre-warmed state. Since curing is, in general, a slow process compared to the extrusion process the curing rate of the compound has to be increased. This can be achieved by using fast curing compounds, at the expense of low scorch safety.

The compound, therefore have to be kept in cold storage.

There is also a pronounced risk of scorching in the extruder. Furthermore high curing temperatures have to be used, which considerably increases the risk for blisters, porosities and deformations during the curing operation.

These risks will be even more aggravated by the fact that continuous curing processes for extruded products works at very low pressures. The problems can, to some degree, be mastered by using compounds with not too low viscosity; by using extruders with vacuum zones and water-absorbing agents (desiccants) like calcium oxide in the compound to avoid gas (steam) formation caused by absorbed humidity.

By coupling together the extruder and the curing equipment facilitates the use of automatic process control and supervision. The curing line can be more efficiently utilized if more than one profile is extruded and cured at one time.

Continuous curing most often imply the usage of more complicated and expensive equipment. Due to the higher productivity a generally higher exploitation of capital and work can be realized.
A pre-condition is however that the curing line has to be utilized to full capacity with long-run series because materials- and/or product change are troublesome and time consuming.

Continuous curing is, as continuous processes in general, easier to supervise and control and normally give rise to higher product quality.

4.8.4 Continuous curing of extrudates

In order to make the manufacturing process more efficient various continuous curing methods have been developed. What they all have in common is that the product, directly after leaving the extruder, continues onwards into a tank or tunnel with a heat-conductive medium.

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

Curing in a salt bath

![Curing in a salt bath](Picture Trelleborg Building Systems)

A salt bath production line (Photo Colmec)
In the salt bath method, the product goes directly via a short conveyor belt down into a tank filled with a melt of liquid salts. The width and depth of the tank varies depending on the size of the products to be manufactured. The length can also vary depending on the available space in the production plant and the processing speeds which are employed. A normal width/depth could be 20 cm x 20 cm with a length of 15 m.

The most common salt mixture used is a blend of sodium nitrite and potassium nitrate with the addition of a certain amount of sodium nitrate, which is heated to a temperature between 180 and 240 °C. During the conveyance through the salt bath, the product must be pressed down underneath the surface with the aid of conveyor belts or rollers.

In the manufacturing of complicated products such as certain rubber profiles, spray nozzles are used to shower the salt mixture over the profiles. In this way the deformation forces from conveyor belts and rollers are avoided. Using high temperatures, the process can be carried out at high speed.

After the curing by the salt bath method, the salt must be washed off and the products must be cooled. Finally the finished product is wound up.

The greatest advantage of this method is that the salt provides very fast heat transmission to the products which are to be manufactured. The disadvantages are the negative environmental aspects of the process.

The salts which are used are classified as toxic substances due to the sodium nitrite content and can, in the event of a fire act as a fuel for combustible materials.

There are stringent requirements on cleaning the rinsing water, which contains a lot of dissolved salt. A common method of purification is to boil off the water and recycle the residual salt. A method that is somewhat gentler to the environment is using a salt where the sodium nitrite is replaced by lithium nitrate.

**Curing using fluidized beds**

![Curing in a fluidized bed (Picture Trelleborg Building Systems)](Image)
Another continuous method, which utilises a tank for curing is the fluidized bed principle. As the name implies, the operation is carried out using a fluidized bed. That is to say the tank, which is somewhat deeper and longer than that used for the salt bath, is filled with glass beads, which are caused to hover by blowing hot air from the bottom of the tank.

The diameter of the glass beads is less than 0.1 mm and the temperature of the air is approximately 220 °C. The hot air is the heat conducting medium and the glass beads provide the conveyance support during the process. There are no conveyor belts since the product being manufactured is carried along by the hovering beads. The method is highly suitable for manufacturing hoses since there are no belts or rollers, which can affect the cross sectional configuration of the product.

The disadvantages are that certain products, such as flat profiles which resemble conveyor belts, can shift the glass beads in the tank. The glass beads can easily stick to certain soft materials, which is why great emphasis is placed on the cleaning of the product. This is done with the aid of revolving brushes and high-pressure washing. After cooling, the finished product is wound up.

Curing with microwaves

Rubber materials have poor heat conductive properties. For precisely this reason UHF heating for continuous curing has been developed. The basic principle is the same as that used in an ordinary household microwave oven. Magnetrones transmit radio waves with a frequency of 2450 MHz, which cause whirl currents in electrical conductive materials and oscillate polar molecular structures in the material.

The movements created in the molecules produce heat. Microwaves are capable of penetrating a few centimetres into the rubber material, which is then heated from the inside out. In the previous processes mentioned above, the opposite is the case heat is conducted from the outside towards the centre.

The magnetrones in the curing equipment are located in a tunnel, which the rubber profile passes through on a conveyor belt. The heat build-up which takes place here must then be maintained in a long hot-air tunnel where the actual curing process takes place. The air temperature in the tunnel is over 200 °C.

Cooling and wind-up then take place in the same way as for other curing methods. In order to make heating with microwaves possible, the rubber material must be
electrically conductive and have polar molecular structures. This is not a problem with the common black reinforced products since they have carbon black as filler. This consists of pure carbon particles, which are electrically conductive and the heating occurs through the induced whirl currents.

If light coloured rubber products are manufactured using the UHF method, some polar material must be added to the rubber compound, such as nitrile or chloroprene polymers. Polyethylene glycol, for example, can also be added to obtain this effect. The heating will however be very much less in light coloured compounds than in black carbon black filled materials.

This curing method is primarily used for thick walled products, which take a long time to cure when using other methods. If there are pollutants in the rubber compound, which can be activated by the microwaves, such as metal filings or poorly distributed carbon black, so-called hot spots may occur. These could get so hot that they ignite the rubber profile while it is being produced.

The same thing can happen if there is an interruption in the feeding of the rubber to the extruder. The amount of material in the UHF tunnel then decreases with overheating as a result. The method makes great demands therefore on the monitoring of the process. Microwave curing has to a certain extent replaced salt baths due to the reduced environmental hazards.

**Curing using shear extruder heads**

![Drawing of a shear extruder head](Picture Trelleborg Building Systems)

At the end of the 1970’s German extruder manufacturers started to develop machines where the heating of the rubber to curing temperature took place in the extruder. Adjacent to the screw, in the normal location for the die, there is a unit called the shear head. It consists of a rotating cylindrical core with a barrel around it. Through the gap formed between the core and the barrel the screw squeezes the rubber material. Because of the generated friction, the material is heated before it reaches the die. Finally there is a hot air tunnel of the same type as in the UHF method to achieve the curing.

The basic idea with the design was that the rubber material would already be somewhat cross-linked when it left the die. The product would then already have a certain amount of dimensional stability on the conveyor belt in the hot air tunnel.

If the method is to be optimised in this way, a great deal of emphasis is placed on the design of the dies to avoid the risk that the curing will take place inside the
machine prior to the die. This phenomenon is usually described by the expression that the rubber material is scorched.

In the shear extruder head, a similar heating process as in the UHF tunnel takes place but without the material being requiring to have a specialized composition.

**Curing using an IR (Infrared Radiation) tunnel**

When manufacturing silicone rubber profiles, curing takes place in a tunnel with IR elements of the sauna heater type, that is to say electrical radiators. By maintaining a high temperature approximately 500 °C, and by using a fast curing material, the tunnel can be kept short. The product cured in the tunnel must then be postcured in a heating oven if the silicone material is to have good heat resistance.

**4.8.5 Continuous curing of cables**

**Curing in steam vessels** is mainly used when curing textile or metal reinforced rubber products such as rubber insulated cables or hydraulic hoses.

Steam tube vulcanisation is based on the principle of the cable or hose being pulled through a long pipe which is filled with a flow of high pressure steam at a pressure of approximately 1.5 MPa which is the equivalent of a temperature of approximately 200 °C. One end of the steam pipe is connected to an extruder.

The steam pipe can be set up both horizontally or vertically. The most common arrangement is when the pipe slopes diagonally downward from the extruding machine and has a shape bent to take into account the bending deformation due to gravity of the product being passed through the pipe. This allows the product being transported to hang freely in the pipe without touching its walls.

This type of production line is called catenary continuous curing (CCV).

The steam tube is normally approximately 60 m long and its outlet is equipped with water-cooling and labyrinth seals in order to prevent an excess of steam from escaping.

The production rate is normally between 10 - 120 m/min. This corresponds to a curing time of 0.5 - 6 min if the steam pipe is 60 m long.

**4.8.6 Continuous curing of calendered products**

**Rotocuring** is used for curing rubber sheeting with or without textile reinforcement, rubberised fabrics and light conveyor belts. In addition, large quantities of flooring materials are produced with the use of the rotocuring method.
Rotocuring is named after the brand name of one of the manufacturers of the machinery. The second important original brand is called Auma. The rotocure machine consists of a large, steam heated, revolving steel drum, which is partly encompassed by an endless steel band. The steel band encompasses approximately 2/3 of the circumference of the drum through the action of two conducting rollers and a tensioning pulley. The drum is heated by means of steam to a temperature of 150 - 200 °C. In addition, there is a heating plate bent round approximately half of the surface of the drum and which gives some additional heat, but primarily it prevents loss of heat.

Calendered rubber material is placed between the drum and the band at the lower conducting roller. With the aid of the tensioning pulley, the band is strained so that a pressure of approximately 0.3 MPa is obtained between the band and the drum.

The linear speed of the drum can vary from a couple of metres up to 200 m of cured material per hour, all depending on the material’s thickness and rate of vulcanisation.

The drum, which is interchangeable, can have completely smooth or patterned surfaces and normally has a diameter of 1 500 mm and a width of between 1 500 - 2 500 mm.

For a normal speed range of 5 - 50 m/h and a contact length against the drum of 3 m, a curing time of between 4 - 35 min is obtained.
### 4.8.7 Radiation curing

Radiation curing means that the rubber material is subjected to high-energy radiation, such as gamma radiation from cobalt-60 or high-energy electron radiation. When the radiation penetrates the rubber free radicals are formed roughly in the same way as with peroxide curing.

The required radiation dose varies for different rubber types from approx. 0.05 MGy to 0.5 MGy.

Gy=Gray, the SI unit of absorbed dose. One Gray is the absorption of one joule radiation energy by one kilogram of matter.

Crosslinking is carried out when the radicals formed by the radiation are combined to give carbon-carbon bonds between the molecules. The cross linking reaction is carried out at much lower temperatures than what is normal in conventional curing.

Certain rubber, such as silicone rubber, chloroprene rubber, nitrile rubber and fluorocarbon rubber, require a relatively small dose in order to be cross linked, while the normal types of rubber require considerably higher doses.

With the addition of certain types of activators, so called sensitizers, the radiation doses can be lowered considerably. 0.05 MGy is often quoted as the highest radiation dose for economical radiation curing.

Radiation curing has not yet had any real practical importance in rubber curing, but certain cable, mouldings, hoses, seals, O-rings and gaskets etc. for very special purposes are cross linked by means of radiation.

The practical use of radiation curing is basically limited to thin rubber layers, and certain cable sheatings and profiles for very special purposes.
The criterias for choosing radiation curing can be influenced by the following drawbacks.

1. The radiation equipment is very complicated and expensive.
2. The sensitizers are expensive which could have a negative impact on the price of the product.
3. Stringent environmental regulations regarding ionizing radiation will require extensive safety arrangements which will make the method rather difficult to use under normal factory conditions.

### 4.9 Latex processes

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

Not only are the processes technological different. Mixing of solid rubber is a fast process when the time needed for latex mixing technique and maturation is very time consuming and can take 2 to 3 weeks.

Natural rubber latex, extracted from the rubber tree Hevea Brasilienses, is the greatest volume of material used. However synthetic polymers, dispersed in water, are used i.e. CR and NBR. They are also named latex.

In principal the processes are the same independent of type of latex.

Several processes are used to manufacture products in the latex industry like:

<table>
<thead>
<tr>
<th>Process</th>
<th>Example of product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dipping</td>
<td>Gloves, balloons, condoms</td>
</tr>
<tr>
<td>Casting</td>
<td>Toys</td>
</tr>
<tr>
<td>Rotational casting</td>
<td>Balls, meteorological balloons</td>
</tr>
<tr>
<td>Extrusion</td>
<td>Thread</td>
</tr>
<tr>
<td>Foaming</td>
<td>Mattresses</td>
</tr>
<tr>
<td>Spreading</td>
<td>Carpet backing</td>
</tr>
</tbody>
</table>

Typical products made through latex technology are:

- Medical products, such as medical gloves, anaesthetic bladders, catheters and blood pressure bladders. The global consumption of natural latex products within the medical care products sector is estimated at approximately 200 000 tons per year.
• Industrial products, such as bellows, protective gloves and isostatic bladders.

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

Bellows manufactured by means of the dipping process (Photo I Atkins)

Surgeon’s gloves manufactured of natural rubber latex

4.9.1 Mixing

Conservation and concentration of the latex is done by the supplier and when delivered it normally has a solid content of 50 to 60 %, It is an alkaline substance with pH 10 - 10.5.
The formulation is very much like a common solid rubber formulation containing:

- Vulcanizing system, normally based on sulphur and ultrafast accelerators activated by zinc oxide
- Stabilizers as fatty acid soaps
- Antidegradants
- Fillers, only not reinforcing like calcium carbonate
- Pigments
- Processing additives, i.e. for viscosity control

Dry chemicals can not be directly added to latex as by doing so the latex will coagulate around the particles. The chemicals must therefore be dispersed in water with the addition of a dispersion agent. In a mill, a ball mill or a colloidal mill, the chemicals are finely ground to an aqueous dispersion.

Likewise processing aids i.e. soap stabilisers and defoaming agents are added after being dissolved in water.

The latex compound is normally mixed in an open receptacle under stirring. The various ingredients must be mixed with great caution and it can take up to three days to complete the mixing process.

The latex compound often requires a maturing period of a week before the further processing process can take place.

### 4.9.2 Dipping

Latex **dipping** is the largest process by user of NR-latex and is used for a wide range of products.

The process contains in principle the following steps:

- Insertion of a mould (former) into the latex compound
- Withdrawing the former
- Drying
- Vulcanizing
- Stripping the product from the former

Prototype and short run formers can simply be produced in wood, plaster or thermoplastics. Formers in such materials cannot always resist the strains which occur during a long run of production.

Production formers are therefore produced in aluminium, stainless steel, ceramics or glass. Certain thermoplastics can also be used.

The surface of the tools can be polished to a smooth finish or coarsely blasted depending on the dipping technique which is to be used and on the properties for which the product is intended.
By making special items in short series a manual operation is often used, but for standard products like gloves, balloons, condoms etc. highly automated systems with high capacity, several thousands per hour, are used.

The variations used in the process can be divided into:

- Straight dipping
- Coagulant dipping
- Heat-sensitive dipping

**Straight dipping** is used for products with a maximum wall thickness of around 0.6 mm.

The process for, i.e. condom manufacturing can be described in a flow scheme as follow:

- Cleaning the formers in water
- Drying and preheating the formers in an oven with air or infrared light
- Dipping of a first layer
- Formers turned around to avoid dripping
- Latex dried in an oven
- Dipping a second layer
- Latex dried in an oven +3
- Bead rolling of 10-15 mm
- Vulcanization in a main oven
- Washing in hot water
- Stripping from the formers by water spray or brushing
- Soaking in water to rinses away harmful ingredients, such as for example processing aids and nitrates from the coagulant compound.
- Surface treatment as chlorination to reduce stickiness and friction
- Testing and packaging

**Coagulant dipping**, which is used for products with a wall thickness up to 1.5 mm (i.e. household gloves) follows the same scheme as above with the exception of the use of a coagulant. The coagulant, which normally is a solution of a calcium salt, is used to dip the formers into prior to the 3:rd step as above and then the formers are dried in the oven again.

The coagulant makes it possible to manufacture products with thicker walls. The thickness is beside the composition of the latex compound even depending on factors like the time the formers are in the latex.

**Heat sensitive dipping** is used for the thickets products with a wall thickness up to 5 mm, i.e. baby nipples and some industrial products.

In principle the flow scheme above is also used for these products. In the process however the dipping former is heated to approximately 60 °C and then dipped directly into a heat sensitive latex compound which contents a substance, normally
a water solution of polyvinylemethylene-ether that at a higher temperature influences on the coagulation of the latex. In addition to this the pH-value has to be lowered to approximately pH 8.0 by using for example formaldehyde.

Irrespective of the dipping technique curing depends on the thickness of the latex coating and on the curing system used in the compound. A curing and drying time of approximately 45 minutes at a temperature of 100 - 120 °C would be a normal guideline.

The thin walled dipped latex products when stored must be protected from light and heat, which both accelerates the ageing process. As a rule, latex products have to be packed so that the renewal of air around the product is minimal and be stored in dark and cool locations.

### 4.9.3 Other processes

**Casting** is used for manufacturing of hollow articles. In the dipping process the latex is placed on the outside of the mould but by casting the latex is placed inside the mould.

Different types of toys are typical products made by casting.

The moulds are made of plaster or for production in big scale of metal i.e. aluminium.

In the process heat sensitive latex is used and the hot mould (around 85 °C) is filled with latex during the time needed to build up the expected wall thickness, usually 5 - 10 minutes. After that time the mould is turned around and the excess amount of latex flows out of the mould. The mould is placed in a curing oven and after approximately 30 minutes the part can be taken out from the mould for further drying and trimming.

**Rotational casting** is used when manufacturing balls and meteorological balloons. In the process, the moulds are filled with a determined amount of latex and the mould is rotated until the inside is covered with latex.

**Extrusion** is used for manufacturing so called elastomeric threads, used for example in the clothing industry. In spite of its name extrusion, the process has nothing to do with extrusion used of solid rubber compounds.

The latex is fed from a container and pressed under constant pressure trough glass spinnerets into a coagulant solution for fast gelling, and then washed, dried and vulcanized in a continuous process.

The diameter of the spinnerets is normally 0.2 to 1.0 mm, and a machine for this manufacturing is making several hundred of threads at the same time.

**Foaming** has earlier been a very important latex technique for producing mattresses, pillows, car seats etc, but the material has more and more been replaced by foamed polyurethane.
The foam rubber technique is in principle a very simple one, though a very sensitive process that needs a lot of control to avoid to much scrap.

The steps are:

- Foaming the stabilized latex by whipping air into it
- The foamed latex is mixed with the other ingredients
- The moulds are charged with the compound
- Vulcanization in steam or air
- Stripping, washing and drying

Spreading of latex is used for backing of carpets whereby the latex is spreaded on the backside with the help of a roller and the excess latex is scraped of with a knife.

### 4.10 Urethane rubber

Of all existing polymer types the polyurethanes are the most versatile. Depending on the basic chemical compounds that the polyurethanes are built up from they can be classified as **thermoplastics, thermoplastic elastomers, thermosets, rubbers, fibres, glues**, and **lacquers** as stiff, half stiff or flexible **cellular plastics**.

The border line between all these variants is not entirely unambiguous. Urethane rubbers are normally considered to comprise the most rubber like variants i.e. normally massive, chemically cross-linked materials with high extensibility. Certain polyurethanes are processed as common rubbers or as thermoplastic elastomers.

The main part of all urethanes rubbers are made and processed like most other polyurethanes i.e based on low molecular, low viscous components. These comprise a liquid resin, usually a low molecular polyester or polyether, a diisocyanate and one or more hardeners that in a stepwise reaction form a cross-linked polymer.
Flow chart for polyurethane manufacturing from liquid components

Blending of the different components that form the mixture, takes place when the materials are in a low viscous state, which facilitates the use of special process techniques. This will be discussed below.

4.10.1 Casting processes

Casting is the classical method to make urethane rubber products. There are numerous casting methods, of which some of the most important will be described.

The first step is to dewater the resin component i.e. removal of the water/humidity. Water reacts readily with isocyanates in the succeeding reaction steps, under splitting of carbon dioxide which causes porosity and blisters.

During dewatering of the resin (polyester or polyether) is heated, usually to 100 – 135 °C, under vacuum to speed up the evaporation. The dewatering process can be done batch wise in simple reaction vessels under stirring, or continuously using thin layer evaporation or spraying.
The next process step is blending of the components that shall react with each other to form the polyurethane. The reaction can be a one-shot type or a two-shot type which results in more or less stable intermediates (adducts or pre-polymer).

It is most common to blend two components, but blends with three or more are also used. The mixing can be done in two different ways: hand mixing or machine mixing.

Batch wise blending, by hand or with the help of a simple propeller agitator, is used for prototype or small-series manufacturing. Machine blending can either be batch wise or continuous. With batch wise mixing the ingredients are fed to a tank with a stirrer using dosage pumps. With continuous mixing the material streams from the dosage pumps e.g. gear pumps passes through a mixing chamber where the components are carefully mixed.
The starting components are stored in thermostated tanks.

After blending, the mixture will have a pot-life of a few minutes up to perhaps half an hour before the mix starts to solidify. Within this time frame the casting has to be finished.

With a long pot-life follows, as a rule, a long hardening- and demoulding time. With a suitable choice of hardeners it is possible to adjust the pot-life to the shortest permissible cycle time for the casting equipment and the product to cast.

The casting itself can be done in many ways of which some will be discussed below.

**Open casting**

Open casting is characterized by the fact that the mixture is poured into an open mould with the opening facing upwards. The moulds are kept at the right temperature by placing them on a heated casting table. With large-series manufacturing, the filled moulds can be conveyed through a hot air oven, where the cross-linking reaction takes place.

The products are demoulded and the moulds are returned to the casting station.

Due to the fact that the casting is pressure less simple moulds, made of aluminium or even polyurethane can be used. The method is suitable for both hand- and machine casting. One advantage is that the method is simple and cheap.

The disadvantages are that porosities and blisters are easily formed and that the meniscus effect creates an uneven upper surface.
**Casting under vacuum or pressure**

Casting under vacuum and pressure is one way to reduce the risk of air entrapments, porosities and blisters. In the first case the mould is filled under vacuum after which the air pressure is let into the mould.

In the second case the mould is filled at ambient air pressure and then placed in an autoclave under pressure.

**Centrifugal or rotational casting**

Centrifugal or rotational casting is another way to minimize the risk of air entrapment, porosities and blisters.

Centrifugal casting in rotating drums with a horizontal axle is a standard method for the manufacturing of polyurethane sheets.

![Centrifugal casting machine for manufacturing of polyurethane sheet](image)

Due to the centrifugal force a smooth upper surface and a blister free material is obtained.

With the same method moulded articles can be made if the moulds are mounted around a rotating axle. The method can also be combined with vacuum in order to further minimize the risk of porosities and blisters.

If the mould is rotated in several planes, hollow articles can be made.

Casting in combination with compression moulding or transfer moulding is still another variant of the casting method.
To compression mould or transfer mould the low viscous material normally will leak out of the mould via the parting line before any substantial pressure is built up in the mould cavity.

When the material solidifies it can go through a plastic stage which resembles un-vulcanized rubber, often named “B-stage”. In this stage the material can be compression- or transfer moulded.

![Diagram of urethane rubber components through casting followed by compression moulding before the blank has hardened](image)

One other way is to cast, in the lower cavity block and wait until a suitable consistency has been obtained after which the upper cavity block is applied and the mould is closed in the same way as for normal compression moulding.

After demoulding most urethane rubber articles has, as a rule, to be post cured at for e.g. 4 – 24 h at 100 – 110 °C to obtain the best mechanical properties.

### 4.10.2 Injection methods

**Reaction Injection Moulding (RIM) or Liquid Injection Moulding (LIM)** detaches itself from common machine casting in so far that the material after mixing is injected in a closed mould which is injected into a closed mould which is fitted in a press in the same way as a common injection machine.

This method can therefore be automized and speeded up in the same way as a common injection moulding process.

Due to the high production rate of this method materials with very short pot-life and hence short demoulding times can be used.

The raw materials are normally heated to a carefully controlled temperature and are transported in heated tubes.

The mixing can be achieved with static mixers, mechanical stirrers or by letting the two material streams, under high pressures being sprayed into each other which cause the streams to be disintegrated and blended. The method is suitable for
making components of urethane plastic as well as urethane rubber. Both massive and cellular materials can be used.

5. Processing methods for thermoplastic elastomers

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

The differences between processing of vulcanised rubber and thermoplastic elastomers may be visualized in following way:

**Rubber process:**

![Rubber process diagram]

Almost all TPE materials are fully compounded by the supplier and delivered as granulate. Therefore no mixing procedure is needed. Neither is curing needed and the scrap can be reprocessed.

These differences lead to lower energy consumption and shorter cycle times for production of TPE products in comparison with rubber products.

As machinery for thermoplastic materials differs from equipment for rubber materials, new investments normally is required when switching the material for a product from rubber to TPE.
Thermoplastic elastomers are normally supplied as granulates in bags and can be used directly to feed extruders and injection moulding machine. (Photo Flexys)

The processes used for thermoplastic elastomers are the following. The two first are the most important.

- Extrusion
- Injection moulding
- Calendering
- Blow moulding
- Melt calendering

5.1 Extrusion

Extrusion is used to manufacture i.e. tubing, profiles and covering of cables. The principle of the extruder is the same as the one of a cold feed rubber extruder.

The most important difference is that the screws in an extruder for thermoplastic elastomers are longer than the common screws for rubber extrusion, with a relation length and diameter (L:D) of 20:1 to 30:1. The longer screw is needed for packing, homogenisation, pressure build up and melting of the granulated material before it reaches the die.

The TPE material is fed into the extruder via a hopper and has to be well dried and free from condense. If any moisture occurs blisters may appear in the ready made product.

The melting temperature is for most TPE materials is in a range from 160 to 240 °C and that temperature has to be reached before the material is passing the extruder.
head. The barrel has normally at least three temperature zones with separate temperature regulation.

The temperature is increased with some 20 to 30 °C in each zone with the highest temperature at the end of the screw and in the extruder head.

The dies used for extrusion of thermoplastic materials are much longer than the dies used by rubber extrusion, and have in many cases a length 10 - 20 times the inner diameter of the die. Furthermore the die is streamlined to improve the material flow.

From the extruder head the product is going into a cooling bath where it will quickly be cold to room temperature with water, often after passing a calibration plate, and winded up.

Scraped products, i.e. with dimension faults, can be granulated in a mill and re-circulated into the extruder.

Recently a so-called “hybrid laboratory extruder” has been developed which can be used for TPE as well as for rubber. Compared with a conventional rubber extruder this machine has:

- Increased screw speed range
- Higher screw torque
- Torque motor
- Special heating/cooling system
- Special screw design

5.2 Injection moulding

Injection moulding is probably the most common process for products made of TPE. Moulded parts of TPE are used in the automotive industry, for shoes, electrical and household’s articles etc.

The technique with injection moulding is very much alike the rubber technique but:

- The screw has a L:D relation like mentioned under extrusion.
- The extrusion part must be heated to the melting point of the TPE type used
- Temperature zones
- The moulds must be cold so the part can solidify

Illustration of the principle:
When the material is injected into the mould the pressure is in the range of 50 - 150 MPa and the injection time is normally below 15 seconds for smaller parts.

Mould shrinkage may occur when moulding rubber, meaning that the ready product is smaller than the cavity in the mould, normally in the interval 0.5 - 2 %.

It is more complicated to control the shrinkage with TPE than it is with rubber as it is highly depending on process variables as pressure, temperature and time, orientation in the material and structural changes in the material.

5.3 Other processes

**Calendering** is only used within limits for TPE. The exception is non-rigid PVC, which can be looked upon as a TPE-material.

The equipment and the process are very much alike calendering of rubber. The main differences are, the high temperature needed and the thinner films made, and calenders used for this purpose are special made.

**Blow moulding** is used for making hollow parts like bottles. The material is extruded into a mould where the shaping is made with the help of an internal air pressure.

**Melt calendering** is used for coating thermoplastic materials on textile. In principle the process is done in a calender with 2 or 3 rolls. The material is feed to the rolls through a hopper and forms a film which is pressed against the textile.
Principle of two roll melting calender

1. Feed hopper
2. Textile off winding
3. Pre heating roll
4. Melting rolls
5. Take off roll
6. Smooth finishing roll
7. Cooling roll
8. Side cutting
9. Winding up

6. Facts of processing methods

6.1 Parameters

The size and shape of many products decide which process to be used and no alternatives are available.

Here are some examples:

- Long length profiles for sealing of windows can only be made by extrusion and preferable continues curing.

- Membranes reinforced with a fabric and shaped in different ways must be compression moulded to keep the fabric in the correct position.
For other products different production methods can be chosen. The choice of the process however requires a good knowledge of both material and processes available. The method one can use depends on many criteria of which the following are the most important:

- **Process ability of compounds fulfilling the product specification**
- **Demands on close tolerances**
- **Demands on fine smooth surface finish**
- **Number of pieces to be manufactured**

Regarding to the compounds it may be difficult to process the material when the requirements on physical and/or thermal properties are very high.

As an example of this a compound with only reinforcing carbon black as a filler and no oil will be very difficult to extrude with a nice glossy surface on the cured product.

A compound of that type, irrespective of what polymer it is based on, can even require an extremely high pressure by moulding and may be difficult to produce by injection moulding due to bad flow in the compound. The only way to process it may be by compression moulding under high pressure.

Demands on close tolerances as well as on smooth finish may exclude processes like extrusion and autoclave curing and require manufacturing by a moulding process.

On moulded products as well as on other products the demands on tolerances and finish influences both on the process and the cost of the mould. On one hand the tightest tolerances and best finish can be obtained by injection moulding which on the other hand requires expensive moulds and put high demands on the process ability of the compounds.

The quantity of pieces to be manufactured is of outmost importance for the choice of a process. If a high quantity have to be manufactured over long time injection moulding should be used if possible. The method offers good opportunities to automate the production, and the high quantity to be produced justifies the expensive moulds giving close tolerances and smooth surface

### 6.2 Choices from different methods

Here follows two examples of products where two ore more production techniques may be used:

**In first case** the product is a flat seal with square cross section, with an outer diameter 25,0 mm and inner diameter 9.0 mm and a thickness of 2,5 mm. Normal tolerances and no special demands on the surface finish is required.
At least three different techniques can be used for the production.

- A 2,5 mm thick sheeting can be calendered, cured in a press or a Rotocure. The sealing is punched from the sheeting.

- A tube with outer diameter 25,5 mm and inner diameter 9,0 mm is extruded on a metal mandrel. Cured in autoclave, grinded to outer diameter 25,0 mm and with the tube still on the mandrel cut into 2,5 mm thick pieces in a lathe.

- Moulding by injection or compression moulding and de-flashed.

By comparing the three different techniques one can state:

<table>
<thead>
<tr>
<th>Method advantages</th>
<th>Disadvantages</th>
<th>To be used</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 no cost for moulds</td>
<td>big scrap volume</td>
<td>low numbers to be made</td>
</tr>
<tr>
<td>2 no cost for moulds</td>
<td>more manual work</td>
<td>by more expensive material or medium volume</td>
</tr>
<tr>
<td>3 efficient manufacturing</td>
<td>mould cost</td>
<td>large volume</td>
</tr>
</tbody>
</table>

The product in the second case is a big sealing ring for a sewage pipe. The ring has an outer diameter of 1 800 mm and the circular cross section has a diameter of 50,0 mm.

The product can either be moulded by compression moulding or it can be extruded as a massive round bolt with the diameter of 50 mm, cured in autoclave or continuously (depending on manufacturing volume).

After curing, the bolt is cut of and spliced in a splicing mould to a ring with outer diameter 1 800 mm.

The best economy will be achieved when using extrusion and splicing. That method does not need any mould costs, and such big mould will occupy a big press but produce only one ring per operation. The cost for the extrusion die will be neglect able in comparison with the costs for a mould.

Extrusion of sealing rings for concrete sewage pipes. After curing in a microwave tunnel, the strip is spliced to form sealing rings. (Photo Forsheda)
6.3 Cost aspects

Already in the step of designing a product, a major part of the final cost can be controlled. Cost for material including mixing is often running up to 60 - 80 % of the total cost for manufacturing a rubber product therefore it is essential to make a proper choice of the material.

As a base for selecting material a specification of the requirements must be done properly and include i.e.

- Mechanical properties

- Minimum and maximum operation temperatures

- Resistance to aging in heat
- Resistance to fluids
- Expected lifetime

As the type of used polymer will control the major cost of the material, tables over polymer properties may be used for the first selection of materials. The major requirements listed as done above will then control the cost in the economical frame that the selected polymer will permit.

Other demands on the product will have a strong influence on the final cost, and among them are the demands on:

- Tolerances
- Surface finish
- Size of flash (on moulded parts)
Especially for moulded parts details in the design will have a huge influence on both mould cost and processing cost. The following items are essential:

**Mould design** - A complicated mould with as few mould parts as possible should be strived for.

**Loading of the mould** - Complex working moments which are making the process more expensive should be avoided.

**De-moulding** - Should be possible to make quick and easy without risk for damaging the product or the mould.

**Trimming** - Designs giving thick flash gives a more difficult and expensive trimming operation.

**Tolerances and finish** - Requirements besides normal for a good function of the product should be sacrificed if it is increasing the cost.

Tolerances and size on flash are international standardized, and are divided into several classes for all type of processes.

In following pictures, suitable respectively and less suitable design of moulded products, are presented. Products with the design given as suitable are alternatively easier to de-mould; giving less flash; or less mould cost.

The total price of the product, as in all calculation in manufacturing, is build up of movable cost and fixed cost.
The **movable cost** includes all kind of cost depending directly of the manufacturing of the part as material, labour cost, cost for machine time, setting up time etc.

The **fixed cost** comprises i.e. depreciation, energy, rent, white collar cost.

### 6.4 Process control

Process control is a part of a company’s quality assurance system which emphasizes on customers needs and to prevent defects and waste by building quality into the product already in design and manufacturing.

Companies are very often certified and operate accordingly to the series of ISO 9000 standards. This is a guaranty that the company is working with a well organized routine in a consequent matter and has well defined responsibility areas.

Process control is set up in the frame of such an organization and is one of the most important parts of the total quality control as it offers control over:

- Raw material
- Compounding
- Semi-manufactured parts
- Final processes

To obtain a reliable process control it is essential to have:

- Well developed specifications for each material and operation
- Correct machines and tools
- Well educated and trained personnel on all levels
- Good commitment from all personnel
- Good motivation from all personnel
To obtain this situation a company needs to have a professional leadership for quality coming from the top management. An organization has to be built up where all personnel are to be given good prerequisite to fulfil the goals for quality. Important strategies to reach the goals are i.e.:

- Training in quality work
- Education of specialists in different functions
- Market orientation, meaning that the customer and the customers need should be in focus
- Program for quality improvements
- Bench marking with the best in the trade

Regarding the machines used in the production it is not always necessary to have the most modern equipment but the machine must be reliable. To ensure correct process parameters it is essential that:

- A preventive maintenance scheme is established for all equipment
- All instrumentation are calibrated on regular bases
- Measuring date are registered and evaluated

6.3.1 Example of measuring and treating of process parameters

**Raw material** – control that it is delivered accordingly to the specification and with a certificate from the supplier (see mixing).

**Mixing** - control of time, temperature and energy consumption, rheometer control on each batch.

**Calendering** - control of feeding, temperature, measurements of wide and thickness.

**Extrusion** – control of temperatures, screw speed, cooling and continuous control of dimensions.

**Curing** - control of temperature, time and pressure.

**Statistical process control** is used to a large extend and is an approach to collect the measurements by using basic statistical methods, normally by utilizing a computer software. Thereby trends can be studied more readily and variations may be diagnosed, controlled and reduced.

The quality system trace the flow through the whole operation and when properly maintained it will contribute to improvements in both quality and productivity.
7. Environment

Preface

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

Localisation

Many industries cause disturbances through noise, transportation and bad smell. These disturbances are magnified when they occur near schools and homes. This problem is not unique to the rubber industry, but localisation issues can sometimes be very difficult to solve. A lot of rubber factories are between 50 to 100 years old. Originally they might have been built on the edge of town, but as the years have passed urban areas have grown up around them.

Communities are now less tolerant about noise, smoke and smell. Many rubber factories have installed cleaning plants to reduce emissions of vulcanising fumes, dust and solvents. Efforts have also been made to reduce noise when working outdoors and from ventilation equipment, machinery, cooling towers and transport.

Contamination of soil and groundwater

In Europe and many other parts of the world, the soil and groundwater have been contaminated by industrial and military activity and by the use of chemicals on farms. In Europe alone there are several hundred thousand polluted areas. Surveying land and then cleaning soil and groundwater are expensive, time-consuming operations. A cleanup can take years and cost millions of euros.

Many rubber factories are old and the land around them shows clear signs of contamination over many years. Leaking underground tanks, accidents, spills from stores and handling of oil and solvents are common causes of soil contamination. Common pollutants are solvents, metals and oil. For many rubber companies, identifying contamination and then clearing it up are everyday activities. These issues come into focus during company acquisitions, sales of industrial land and factory closures.

Consumption of natural resources – raw materials in a life-cycle perspective

The extraction of raw materials and production processes in the polymer industry have several different types of impact on the environment. Some impacts occur at the production site while others occur during the extraction of raw materials, transportation and the handling of waste. The following paragraphs deal with the environmental impact of the key raw materials and processes. The substances that are of special interest are as follows:
Natural rubber

The rubber tree (*Hevea brasiliensis*) requires a tropical climate. Today, more than 90% of all natural rubber comes from South-East Asia, although there are also plantations in South America and Africa. Nearly 70 percent of natural rubber production is used in the tyre industry. About 80 percent of natural-rubber production derives from small-scale operations conducted by local growers. Typically, an area of rainforest is cleared and rubber trees are planted. As a result of such methods, the original tree species disappear and are replaced by a monoculture of rubber trees.

However, other types of plants gradually regenerate to a certain extent. A rubber plantation usually has a density of 200 to 500 trees per hectare. It normally takes from four to seven years before the tapping of the trees for their sap (latex) can begin. One tree produces approximately 2 kg of latex each year over a period of 25 - 35 years. The yield is affected to a considerable degree by cultivation techniques, soil conditions, use of biocides and the addition of nutrients. The chief by-product from the rubber plantation is timber from the trees, which is mainly used as firewood, but it has also been exported in recent years for use in the manufacturing of furniture and flooring.

Latex consists of water, rubber polymers (about 33%) and a number of other substances, including proteins. Around the rubber polymers there is a layer of proteins that prevents the latex from forming clumps. Latex must be processed to preserve and concentrate it. Ammonia and formaldehyde are added to prevent premature coagulation. After this processing stage, the raw material is usually transported to a plant, where acetic acid or formic acid is added to make the latex coagulate. The latex is then dewatered and the solid product is dried. An overview of the production process for natural rubber shows that the environmental impact
derives from clearing the forest, the use of energy, chemicals, nutrients and biocides, and from emissions to water.

Production of natural rubber

**Synthetic rubber**

About 60 % of world production of synthetic rubber is used for tire manufacture. Synthetic rubber is a product of the petroleum industry. Styrene-butadiene rubber (SBR) is the most common type of synthetic rubber and has similar characteristics to natural rubber, however the rubber industry uses a large number of synthetic rubber polymers that have varying characteristics. The environmental impact from the production of synthetic rubber derives primarily from energy consumption, emissions to air and water, and waste products.

**Environmental impact of other components in rubber**

The rubber industry uses thousands of recipes and a large number of different chemicals. Table below provides an overview of the environmental impact of the most common components.
Consumption of natural resources – energy and water

One of mankind’s greatest challenges is to maintain consumption of natural resources at levels that are sustainable in the long term. Our dependence on fossil fuels such as coal and oil is frighteningly large and the availability of clean water in sufficient quantities is limited in many countries.

Energy consumption

The greenhouse effect

The Earth’s average temperature is around 15 °C. The temperature is increasing because some of the gases in the Earth’s atmosphere (mainly steam and carbon dioxide) have a tendency to absorb heat radiation. This is just like how glass panels in a greenhouse capture some of the heat radiation being emitted from Earth back into space. These gases have always been in the atmosphere, but several of them are now present in increasing amounts. The evidence suggests that the greenhouse effect is growing and that the average temperature of the Earth is rising. The level of carbon dioxide in the atmosphere is now around 30 % higher than it was 200 years ago, and it is increasing at around 0,4 % per year. The burning of fossil fuels (coal, oil, natural gas) is contributing to this increase. In addition to

<table>
<thead>
<tr>
<th>Substance</th>
<th>Production methods and environmental impact from a life cycle perspective</th>
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<tbody>
<tr>
<td>Carbon black</td>
<td>Carbon black is produced through pyrolysis or through combustion processes in furnaces. The furnace-black process consumes approximately 1,6 tons of aromatic extracts and 0,2 tons of natural gas to produce 1 ton of carbon black. Carbon black is a black powder with highly polluting characteristics. Other environmental effects include energy consumption, emissions to air and waste from the production process. Suppliers in several countries produce the substance in a process involving energy recovery. They provide bulk delivery using reusable containers.</td>
</tr>
<tr>
<td>Accelerators and anti-degradants</td>
<td>In rubber industry processes, accelerators and anti-degradants make up approximately 1 - 1,5 % of the weight of the rubber mix. Substances such as 6 PPD and CBS are hazardous to health and highly toxic to aquatic organisms. Since accelerators and anti-degradants are produced in relatively closed processes, they are not emitted to the external environment. However, fairly significant emissions of various hydrocarbons to air and water have been reported.</td>
</tr>
<tr>
<td>Sulphur</td>
<td>Sulphur is produced mainly as a by-product in refineries that process crude oil and natural gas. In the process, elementary sulphur is formed from hydrogen sulphide. The environmental impact is in the form of energy consumption, emissions to air and water, and waste products.</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>Roughly half of world production of zinc oxide is used in the rubber industry. A number of different methods are used to produce zinc oxide. Previously, it was produced mainly from zinc ores extracted from zinc mines, but recovered metallic zinc is now an important source. Production of zinc oxide causes environmental impacts resulting from mining operations, emissions to air, energy consumption and waste generation. Zinc oxide is toxic to aquatic organisms.</td>
</tr>
<tr>
<td>Aromatic extracts</td>
<td>The aromatic extracts used in the rubber industry derive mainly from the production of lubricating oils. Since the aromatic carbon compounds contained in the crude oil do not have good lubricating properties, they are extracted during processing. The solvent lutilal is normally used as the extraction agent in the process. The aromatic extract can be viewed as a by-product of the petroleum industry that has come into extensive use in the rubber industry. Aromatic extracts are toxic and classified as carcinogens due to their content of polynuclear hydrocarbons (PAH). The environmental impact from the production of aromatic extracts is primarily in the form of energy consumption, emissions to air, and waste products.</td>
</tr>
</tbody>
</table>
carbon dioxide, other greenhouse gases are being emitted in larger amounts now than before industrialisation. Nitrous oxide (laughing gas), methane and tropospheric ozone are just some of these greenhouse gases generated by human activity.

Reducing mankind’s impact on the climate is primarily about reducing emissions of carbon dioxide via the burning of fossil fuels. The use of coal, oil and gas for heating, energy production and transport is the key source of emissions.

**The rubber industry and greenhouse gases**

Consumption of fossil fuels for heating and production processes in the rubber industry is relatively high. Emissions of carbon dioxide are also high therefore. For example, the Trelleborg Group emitted 140 000 tons of carbon dioxide due to energy consumption in 2003. Emissions from the transportation of raw materials and finished products also add to carbon dioxide build-up. The use of certain products, such as tyres, also adds to emissions through the fuel consumption of vehicles. A life cycle assessment (BLIC, 2001) shows that the rolling resistance of a tyre has a significant effect on its environmental impact. Increased resistance means higher fuel consumption and thereby higher emissions of carbon dioxide. On the positive side of the carbon dioxide equation, it must be noted that the trees on rubber plantations consume carbon dioxide.

Over the years many rubber factories have introduced measures to make themselves as energy-efficient as possible. There are many good examples of how these measures have resulted in significant reductions of energy consumption. The forces driving energy savings remain strong. High energy prices and trading of carbon dioxide emission quotas, for example, mean that production and distribution processes must be rationalised even further.

**Water consumption**

The rubber industry consumes water for cooling, processes (e.g. phosphatising of metals) and sanitation. Water consumption during the production process for natural rubber is considerable. However, many factories have been able to cut consumption by introducing cooling-water recirculation systems.

**Use of chemicals**

The production of rubber products requires a large number of raw materials and chemical products to achieve the required properties. Many of the chemicals used are relatively harmless from an environmental or health perspective. However, there are a number of substances that can damage the environment and injure humans. Some of these substances are classified as environmental toxins.

**Environmental toxins**

Environmental toxins have certain characteristics in common. Some of them are extremely toxic and can prove fatal even in small doses. Others do not kill, but they can cause serious injury to living organisms in small doses. One reason for this is their stability, which means that they persist for a long time in natural conditions. Toxins can therefore spread across wide areas before they break down. If substances can also be stored in living tissue (bio-accumulation) then there is
increased risk for biological damage. If an organism is unable to biodegrade the chemical there is a risk that contamination can accumulate in the fatty tissue of the organism.

![Image](Photo T Brorson)

The highest levels of toxins are found, therefore, in mammals and birds that live on fish or other seafood.

Many aromatic hydrocarbon compounds are both fat-soluble and persistent. If these substances are halogenised (i.e. if their hydrogen atoms are replaced with chlorine, bromine or some other halogen) then both stability and fat-solubility increase further. In some cases toxicity also increases. Several well-known organic toxins belong to this group of halogenated aromatic hydrocarbons. Heavy metals can also be toxic. Industrial chemicals that were never intended to enter the natural environment can leak into the environment anyway. PCBs (poly-chlorinated biphenyls) used in transformer oils, electrical cables and many other places are probably the best-known examples. Other industrial chemicals found in the natural environment are chlorinated paraffin and brominated flame retardants. Some of these substances are no longer manufactured. PCB, for example, is prohibited in many countries. Other substances have proved to be more difficult to replace with less dangerous substances. For example, the use of brominated flame retardants continues unabated for this reason.

The rubber industry and environmental toxins

Organic substances are used in the vulcanisation process in the rubber industry to give products the desired properties. These substances include accelerators, softeners, antioxidants and flame retardants. Table below provides an overview of the main groups of substances and their properties.
Heavy metals

Some metals are hazardous for living organisms. This is especially true for certain heavy metals in high concentrations. Part of the problem is that several of these heavy metals can be stored in living tissue and remain there for a long period. Heavy metals are usually considered to be elements with density above $5\,\text{g/cm}^3$. There are relatively few that crop up in an environmental perspective.

The most-used metal in the rubber industry is zinc. As zinc oxide and other compounds, zinc is found in most rubber products. Zinc is toxic for water-based organisms, and public authorities have noted that zinc is spread throughout the natural environment via the wear of car tyres on roads. At present there is a very limited possibility of replacing zinc with another substance in rubber products. Lead was once common, but its use has decreased. The vulcanisation of certain types of rubber tubing is still performed by heating lead in a closed system. Cadmium, copper, chrome and other heavy metals are also present in other applications.

Emissions to air

The rubber industry affects the surrounding atmosphere through various types of emission from energy consumption, production processes and the transportation of raw materials and finished products. Much of the contamination is similar to that

<table>
<thead>
<tr>
<th>Function category</th>
<th>Substance group (example in brackets)</th>
<th>General assessment of environmental and health properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accelerators</td>
<td>Dithiocarbamates, (Ziram)</td>
<td>• May be toxic for aquatic organisms</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• May form carcinogenic nitrosamines</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• May be allergic</td>
</tr>
<tr>
<td>Thiazoles, (MTB)</td>
<td></td>
<td>• May form carcinogenic nitrosamines</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• May be allergic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• May be toxic for aquatic organisms</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• May be persistent in the environment</td>
</tr>
<tr>
<td>Thio carbamides,</td>
<td></td>
<td>• May be toxic</td>
</tr>
<tr>
<td>(ETU)</td>
<td></td>
<td>• Suspected as carcinogenic, and having</td>
</tr>
<tr>
<td></td>
<td></td>
<td>teratogenic and reproduction toxic properties</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• May be allergic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• May be persistent in the environment</td>
</tr>
<tr>
<td>Thiram sulfides,</td>
<td></td>
<td>• Toxic for aquatic organisms</td>
</tr>
<tr>
<td>(TMTD)</td>
<td></td>
<td>• May form carcinogenic nitrosamines</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• May be persistent in the environment</td>
</tr>
<tr>
<td>Antioxidants</td>
<td>p-phenylenediamines, (6PPD)</td>
<td>• Highly toxic for aquatic organisms</td>
</tr>
<tr>
<td></td>
<td>Butylphenols, (BHT)</td>
<td>• May be persistent in the environment</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Highly toxic for aquatic organisms</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• May be persistent in the environment</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• May have high potential to bioaccumulate</td>
</tr>
<tr>
<td>Flame- retardant</td>
<td>Chlorinated paraffins</td>
<td>• Persistent, bioaccumulable</td>
</tr>
<tr>
<td>materials</td>
<td></td>
<td>• Create environmentally hazardous</td>
</tr>
<tr>
<td></td>
<td></td>
<td>transformation products</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Toxic for aquatic organisms</td>
</tr>
<tr>
<td>Softeners</td>
<td>Phtalates, (DEHP)</td>
<td>• Suspected of having reproduction- and</td>
</tr>
<tr>
<td></td>
<td></td>
<td>hormone-disturbing properties</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Some may bioaccumulate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• May be toxic</td>
</tr>
<tr>
<td>HA oils</td>
<td></td>
<td>• Contain carcinogenic PAH.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• May be persistent</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• May have the potential to bioaccumulate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• May be toxic</td>
</tr>
</tbody>
</table>
caused by other traditional industrial processes. However, emissions from the vulcanisation process are unique to the rubber industry. An overview of the general and specific atmospheric pollution caused by the production and processing of rubber products is given below.

Greenhouse gases

The emission of carbon dioxide due to the consumption of fossil fuels is considerable in the rubber industry. The effects are described in the paragraphs above devoted to energy issues.

Acidifying substances

Since the end of the 19th century rainfall has become more acidic. One of the reasons is the emission of sulphur dioxide from the burning of fossil fuels (oil, coal) in connection with energy production, industrial processes and transport. In addition to sulphur dioxide, acidifying nitrogen oxides are generated during various combustion processes. A large part of these emissions are made by cars and they are a major cause of the acidification of soil and water.

The rubber industry also contributes to the acidification of soil and water by emitting sulphur dioxide and nitrogen oxides, mainly though the burning of fossil fuels and emissions from transport. The use of heating oil with low sulphur levels means significantly lower levels of emissions. Conversion to natural gas is helping to minimise emissions of sulphur dioxide.

Ozone-depleting substances

In the stratosphere 10 - 50 km above the Earth’s surface, sunlight onverts some of the oxygen molecules (O₂) in the air into ozone (O₃). The ozone layer thus formed absorbs ultraviolet light from the sun (UVB radiation) and the result is natural protection against harmful ultraviolet radiation.

Over several decades, emissions of chlorofluorcarbons (CFCs or freons) have caused a thinning of the ozone layer. The most extensive damage to the ozone layer has occurred over Antarctica. One of the consequences has been that harmful UVB radiation is reaching the Earth’s surface in greater amounts. A relatively small increase in radiation is already making certain species grow more slowly. Plankton algae, which does not have the same outer, protective layer of cells that other plants have, are especially sensitive. Higher levels of UV-B radiation can damage the human eye (cataracts) and affect the immunity systems of both humans and animals.
Several international agreements have helped reduce the use of ozone-depleting substances. The industrial world stopped producing halons in 1994, and since 1996 there has been no production of CFCs, carbon tetrachloride, or 1,1,1 trichloroethane. The use of methyl bromide will be phased out, with certain exceptions, in industrialised countries by 2010, and HCFC production should cease by 2030. Unfortunately, production is still increasing in certain developing countries. Furthermore, CFCs, halons and similar substances will continue to leak from old products and plants for many years in the future.

The rubber industry has used ozone-depleting substances for some time because of their physical properties and chemical stability. In accordance with environmental legislation, several substances now been replaced with new ones or with new technology.

- CFCs, carbon tetrachloride and 1,1,1 trichloroethane were previously used as solvents in the rubber industry, but have now been replaced with perchloroethylene, water and hydrocarbons. Water-based compounds or hydrocarbons are often used to degrease metal parts.

- CFCs were previously used in fridges, cooling plants, heating pumps and air conditioning systems. They has now been replaced by ammonium hydrate, hydrocarbons or HFC.

- The production of polyeuthethane foam materials no longer requires CFCs or HCFCs. Hydrocarbons, HFCs or carbon dioxide are used instead.

- Halon 1301 has been used in aircraft, military applications, computer plants and general industry. New fire extinguisher systems use stable gases or gas mixtures (argon, nitrogen and carbon dioxide) or water vapour.

**Emissions that cause low-level ozone**

Ozone belongs to the photochemical oxidants that are formed at low levels of the atmosphere through the reaction between sunlight, nitrogen oxides (Nox) and hydrocarbons (VOC, volatile organic compounds). Both nitrogen oxides and hydrocarbons occur naturally in the atmosphere but levels have risen due to human activity. As a result, ozone levels nearer ground level have increased. In Europe the concentration has doubled since the end of the 19th century. Emissions of nitrogen oxides and hydrocarbons are mainly caused by traffic and power plants. Emissions of solvents (VOC) from industry and petrol stations also contribute to the build-up of low-level ozone. Nitrogen oxide and hydrocarbon emissions must be limited in Europe. It can be achieved by installing catalytic converters on cars and by manufacturing plants reducing their emissions of solvents. A lot of work still needs to be done before ozone levels are changed significantly.

Within the rubber industry several substances are handled that contribute to the build-up of low-level ozone. Organic solvents are used in some processes. Transport and the burning of fossil fuels are other sources of emissions. The vulcanising process also results in the emission of hydrocarbons.
Emissions that cause localised air pollution

Heavy traffic, the burning of oil and wood and emissions from industry mean that the air in many urban areas is of poor quality and constitutes a health risk. Heavy traffic is the main cause of emissions of hydrocarbons, carbon monoxide and nitrogen oxides. Major efforts have therefore been made to reduce hazardous emissions from cars, trucks and buses. The most successful effort so far has focused on reducing the lead content in car exhaust emissions. Catalytic converters also mean lower emissions of other contaminants. Road traffic has continued to increase, however, and many older cars without catalytic converters are in use. Diesel engine exhaust emissions are harder to clean than petrol engine exhaust emissions. Even though restrictions have got tougher, emissions from diesel powered vehicles account for a growing proportion of the hazardous substances found in the air in urban areas. Diesel exhaust emissions contain carcinogenic hydrocarbon compounds (PAH) and microscopic particles which increase the risk to human health. The wear of studded tyres on roads also adds to the amount of particles in the air in urban areas. Normal rubber tyres also contribute to particle build-up.

For historic reasons many rubber factories are located in central urban areas and are surrounded by housing. The rubber industry adds to air pollution through the emission of vulcanising fumes, solvents, dust, nitrogen oxides, sulphur oxide and odorous substances. It is quite common for neighbours and the authorities to express their opinions about rubber factory emissions. The levels of harmful substances are generally considered to be low, but most people dislike the typical rubber smell. The authorities have looked at the composition of vulcanising fumes and assessed their effect on humans and the environment. Vulcanising fumes contain benzene and other air pollutants. In view of the fact that the fumes contain a large number of substances that are hazardous to the environment and to human health (albeit in low concentrations) it has been thought prudent to demand that rubber companies install air-cleaning equipment.

Waste

Annual world consumption of rubber is in the order of 15 million tons, of which natural rubber accounts for around 38 % and synthetic rubber for around 62 %. Around half of all rubber is used for the manufacture of car tyres, while the remainder is used in a wide range of products. About 2 million tonnes of tyres are scrapped each year in Europe and around 2,8 million tonnes in the US. Other rubber products also eventually become waste, and the quantity of waste rubber worldwide is substantial. Incineration of waste rubber is common in many countries. By using rubber as an auxiliary fuel in cement plants and heating plants, the fuel value of the waste can be utilised. However, large quantities of waste rubber still end up as landfill. Recycling methods that are applied to some extent to tyre and production waste include the reuse of scrap rubber in the form of finely ground powder in various rubber materials, and the mixing of rubber waste into asphalt. Chemical recovery methods are also used to a limited extent. Examples of these methods include pyrolysis, devulcanisation and the production of reclaimed rubber. The problem, however, is
that vulcanisation is an irreversible process, which hinders both the reuse of rubber material and the recycling of output material.

Demands for technical solutions to deal with rubber waste will increase because a ban has been imposed (within the EU) on depositing unsorted combustible waste in landfills. Since both non-vulcanised and vulcanised rubber belongs to this waste category, the rubber industry can expect waste-management difficulties in a number of countries. The costs of waste management are also rising dramatically in some countries. From both a cost and an environmental perspective, waste issues are very important for the rubber industry. In addition to specific rubber waste other types of waste are produced at rubber factories, such as packaging waste, hazardous waste, waste metal and building waste.

### 7.1 Health and safety

**You don’t go to work to get hurt**

The human body and physical conditions have not altered much over the past 20 000 years. The development from hunter-gatherer to farmer around 8 000 years ago was made possible by cultural changes. Man built the industrial society by developing tools, aids and machines. Each generation has made continuous improvements and tools have been enhanced. Industrial development has placed new demands on humans, however. Many of us spend a large part of our lives sitting down, and when we use our bodies we often do so monotonously with an exaggerated concentration on one part of our body. Although most workplaces have been improved through technical and organisational measures, there are still many working environment factors that can be harmful. Exposures to chemical substances, noise, heavy lifting, stress are just some examples. The working environment of the rubber industry has also improved, but there is still a lot that can be done to make things even better.

Noise, workplace climate, lighting, radiation and vibrations are examples of **physical factors** in the working environment. Physical factors can cause human injury, but they can also affect comfort and performance. Working in a badly lit, noisy and hot area is highly demanding for most people. Physical factors can combine and reinforce negative feelings in the working environment and thus increase the risk of an accident occurring.

The working environment can also entail risks involved with exposure to **chemical substances**. Every year thousands of work-related illnesses are reported which are thought to be linked to chemicals. The most common are eczema, asthma and other allergies. Many work-related accidents are also reported each year which are caused by chemicals. Injuries are caused by spilling, splashing or inhaling of chemicals. Fire, spills, leaks and explosions involving chemicals can have serious health and environmental consequences. Chemicals are also associated with cancer, nervous system disorders, damage to plant and animal life and other chronic diseases.
Accidents in the rubber industry

Working with rubber and other polymers entails exposure to work environments that can give rise to both injuries and illnesses. Work environments of special interest are:

- Exposure to chemicals, solvents and vulcanising fumes.
- Heavy lifting and repetitive tasks.
- Noise.
- High temperatures in workplaces and burns caused by hot equipment.
- Cuts and crushing injuries.

Compared with other industries the frequency of accidents is higher in the rubber industry than in other industries. Figure below gives examples of the frequency of different types of accident at a large rubber factory. In many cases the injury is limited and results in just one or two days of sick leave. Some injuries can lead to long leaves of absence, however.

Health risks in the rubber industry

The rubber industry identified the health risks for its workers many years ago. The incidence of certain cancers aroused the attention of researchers and companies. As a result the industry implemented measures to reduce the risks, such as improved ventilation, the replacement of certain hazardous substances and increased use of safety equipment. Despite all these measures and considerable research, a lot of key questions remain about any alleged connection between certain illnesses and the working environment of the rubber industry. Since the 1970s around 50 epidemiological surveys have been performed, but the chemicals have not yet been identified that cause a higher frequency of cancer in the rubber industry. One problem is that there are many different substances in the working environment and it is difficult to pinpoint exactly how people are exposed to them.
In addition to the risks associated with handling hazardous substances, injuries caused by repetitive physical lifting are common (see figure below). Heavy lifting and repetitive work sooner or later damage people’s mobility and such work is relatively common in the rubber industry. Furthermore the noise level in many workplaces is high. The risk of damaged hearing is significant when working close to noisy equipment.

Examples of work-related illness in the rubber industry (not included cancer) (T Brorson)

The good work

There are limits to working hours, noise levels, use of chemicals and other factors in the working environment. There are no comparable limits for psychological and social effects. However, there is a lot of knowledge about the factors that create a good working environment. The following five factors are usually considered significant in this respect:

- **Autonomy of work.** Each individual should have the opportunity, within limits, to influence the distribution, pace and method of working. No one need be completely controlled by another person or by the technical system. In this regard it is not better to be controlled by a machine than by another person.

- **Positive work climate.** Your immediate superior plays an important role in creating a good atmosphere. It is important to receive praise, of course, but it is also important to receive the right information and have the opportunity to give your views.

- **Stimulating assignments.** A stimulating job gives the individual the opportunity to use and develop knowledge and skills. Learning new things is often greatly valued.
• **Good fellowship.** The organisation should create the conditions for cooperation and social contact. Enjoyment and fellowship reduce stress and prevent conflicts.

• **Reasonable workload.** It’s not easy to define what exactly is a reasonable workload. Some people say that their body cannot take too much work, while others can remain active all day long. The workload should be optimum both physically and mentally, i.e. it should be challenging but manageable. Nobody feels good by being overburdened or under-utilised.

Unfortunately, there are too many workplaces that do not live up to demands for sensible and worthy working conditions. People who work in poor conditions react sooner or later. Anger, dejection and reluctance to co-operate are the normal reactions. If problems persist, stress symptoms can develop. Problems at work tend to spill over into life away from work. A poor working environment can thus impact negatively on families and leisure time.

**Systematic work to improve the environment and the working environment**

To reduce risks for the environment and to improve working conditions many companies nowadays follow environmental and occupational safety management systems. Many companies attain certification in accordance with the ISO 14001 environmental management standard (see figure below). Work aimed at introducing management systems for the working environment (OHSAS 18001) is underway at many sites. The experience of these systems is positive and internal and external audits help the company to focus on the key environmental and occupational safety aspects.

![The basis elements of ISO 14001](image)

**7.2 Recycled rubber**

Due to fairly high costs and technical difficulties to recycle used rubber products, the reuse of recycled rubber in new compounds is limited. However, the products discussed below are important as raw materials for rubber manufacturing.
**Reclaim**

In the beginning of last century, a technique to break down old tyres to a curable product was developed. The new material was named reclaim. Reclaim is mainly manufactured from waste tyres. The tyres are crushed and under influence of heat, chemicals and mechanical work they are broken down to a curable material, which after the chemical process is refined on mills. The textile and metal parts are removed during the process. During the wars in the 20th century, when there was a lack of new rubber polymers, reclaim was then a very important raw material.

Due to both economical and environmental concerns, the importance of reclaim made from tyres has decreased. To some extent the usage is following the oil price. Increased oil-price makes SBR more expensive and by that the reclaim more attractive. Reclaim made from inner tubes for tyres, made of butyl rubber, is an important raw material when manufacturing inner tubes. Reclaim of nitrile rubber, based on scrap from manufacturing of oilresistant products, is likewise important for manufacturing of many technical oil resistant products, mainly moulded.

**Rubber crumb**

While the interest for tyre reclaim has decreased, the use of rubber crumb when manufacturing new rubber products has increased. Rubber crumb is manufactured either from crushed tyres, where textile and steel parts have been separated, or from buffed treads from retreading operations. Most crumbs on the market is made from buffing, as that process is cheaper than crushing tyres and separating textile and steel.

The common method is to grind the rubber at room temperature. The first grinding procedure gives granules in size 1 – 5 mm, which can be used for i.e. sport tracks. When a second grinding is made, that can be done either in a wet grinding process or by cryogenic grinding (cryogenic means cooling with liquid nitrogen), a powder with particle size down to 0,1 mm is received. This fine particle size powder can be used in fresh rubber compounds.

By adding the crumb to a compound, the general rule says, that a decrease of mechanical properties by 1 % will be the result of adding 1 % powder. A non-treated rubber crumb can therefore, only be used in low proportions in rubber compounds, normally maximum 5 – 10 %.

Some special purpose types of rubber like fluorocarbon rubber and silicone rubber may be ground to very fine particles, and can be used in rather high proportions in fresh compounds. The reason is that adding cured ground rubber of the same type will not influence these polymers specific properties, like heat and chemical resistance. Today products are available in fluorocarbon rubber with good properties that are made totally from rubber powder.
Surface treated rubber crumb

Different processes are developed to treat the surface of the rubber powder and thereby improving the bonding of the powder to the other ingredients in the compound. The common type of modification is to add a low molecular weight polymer. This has made the use of crumb interesting, not only for decreasing compound costs but also to achieve improved properties for both the manufacturing process and for the end product. For products with requirements on good abrasion resistance, crumb made from truck tyres is used and the good wearing properties can be kept. The processing properties are very often improved by adding some parts of crumb. For example it is easier to extrude a tyre tread containing some crumb, and by moulding it is easier to get rid of trapped air, which will give less defects and scrap.

The table summarizes raw materials from scraped rubber used in the rubber industry

<table>
<thead>
<tr>
<th>Initial product</th>
<th>Process</th>
<th>Raw material received</th>
<th>May be used in</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste tyres</td>
<td>Chemical breakdown + refining</td>
<td>Tyre reclaim</td>
<td>Tyres, hose, sheeting</td>
</tr>
<tr>
<td>Buffings</td>
<td>Grinding</td>
<td>Rubber crumb</td>
<td>Sheetling, tyres, hose</td>
</tr>
<tr>
<td>Buffings</td>
<td>Grinding + surface treatment</td>
<td>High quality crumb</td>
<td>Tyres</td>
</tr>
<tr>
<td>Scrap from manufacturing of NBR products</td>
<td>Heat breakdown + refining</td>
<td>NBR reclaim</td>
<td>Moulded products, hose</td>
</tr>
<tr>
<td>Inner tubes of Butyl rubber</td>
<td>Heat breakdown + refining</td>
<td>IIR reclaim</td>
<td>Inner tubes, moulded products</td>
</tr>
</tbody>
</table>