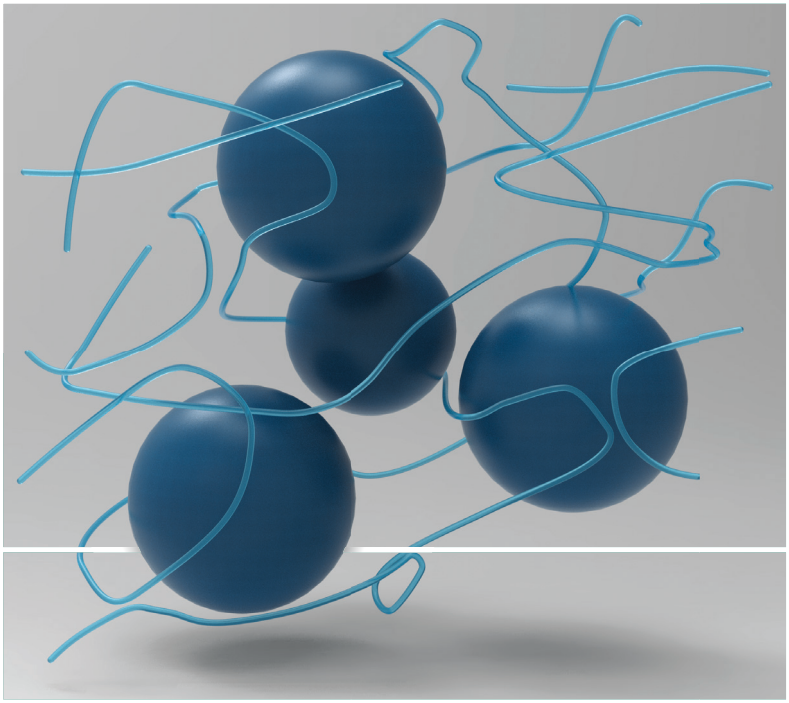
Robert H. Schuster

Reinforcement of Elastomers by Nanoscaled Fillers

Carbon Black, Silica/Silane, Carbon Nanotubes, and Layered Silicates



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The Author

Robert H. Schuster studied Organic Chemistry at the "A. I. Cuza" University in Jassy, Romania, and obtained his doctorate degree at the Institute of Macromolecular Chemistry in Freiburg, Germany. From early 1984, he worked at the German Institute for Rubber Technology in Hanover, which he headed from 1992. During this time, he enjoyed good cooperation with Prof. Jacobi from the State University Porto Alegre (Brazil). The author has been a professor at the University of Hanover since 1995. The institute is involved in national and international projects with raw material manufacturers, the rubber industry and customers. The institute has six departments through which more than 70 doctoral students find their way into the rubber industry. Topics covered range from filler reinforcement, rubber blending, vulcanization, physical properties, magnetic elastomers, rubber-filler composites, electrospinning fibers, magnetic elastomers, investigation of physical properties and fatigue. An essential part of the work is the study of carbon black, silica, silanization of silica, wet-mixing of layered silicates and carbon nanotubes. After leaving the DIK, the author collaborated with Lanxess AG and with the EVE Institute of Dr. M.-J. Wang in Qingdao. Over the years, the author has participated in DKG Meetings and ACS Meetings and Conferences around the world. Over his career in rubber research, Robert H. Schuster has published more than 300 scientific papers, two books and five book chapters and is coauthor in several German Patents. In 1995 he received from the DKG the Carl Dietrich Harries medal and in 2011 from the Rubber Division the Melvin Mooney Award.

Preface

Elastomers are fascinating and indispensable materials for society. They make a huge contribution to our safety and comfort in the world of mobility. Based on the unique principle of entropy elasticity, elastomers cannot be replaced by any other class of material. Their performance, functionality and quality depend on the selected raw materials, especially rubber and filler, on mechanical mixing to form homogeneous compounds, and on efficient crosslinking. Some topics have been studied intensely and have led to technological progress. There is no doubt that the reinforcement of elastomers with nanoscaled fillers is one such topic. Therefore, the nanoscaled fillers are important due to their availability to improve the physical properties of elastomers. The use of nanoscaled fillers in rubber compounds is a multidisciplinary task that requires a knowledge of how to produce the filler particles, of how to mix them with the rubber, of how to disperse them and of how they enhance physical and dynamic-mechanical properties while reducing elastomer rupture.

Reinforcing fillers increase abrasion resistance, ensure low wear and a longer service life, as well as confer useful dynamic-mechanical properties on elastomers. In order to be able to describe and predict these properties, it is necessary to understand that the degree to which a filler is dispersed during mixing is a quality parameter. With the dispersion of each filler, rubber-filler interaction is improved, an effective phase connection between filler and rubber is achieved and thus the mechanical properties and the service life of elastomers are increased. The importance of filler dispersion as a material-determining parameter of elastomers increasingly became the focus of technological and scientific interest as high-performance elastomers were developed: The properties of rubber and fillers were improved and harmonized, more-efficient mixing technologies were developed and the rubber-filler interaction was studied extensively and systematically to deepen our understanding of it.

The book compares how different fillers are used to provide reinforcement for rubber: carbon black, silanized silica, layered silicates, and multi-walled carbon nano-

tubes. The fillers offer a variety of reinforcement options that can be used and expand the applications of the elastomers. Regarding the impact of the different fillers on the aspect of rubber reinforcement, filler properties, such as aggregates morphology and the aspect ratio play an outstanding role in filled elastomers. The book explores how combining conventional fillers such as carbon black or silanized silica with small amounts of high-aspect-ratio fillers creates hybrid fillers that offer new properties which cannot be achieved with conventional fillers. It is explained in great detail how the rubber-filler interaction affects the physical, dynamic and fatigue properties of rubber. The presented chapters emphasize a consistency, providing an overall picture of rubber reinforcement.

This book draws on the author's longstanding experience with the global rubber community and is aimed at rubber technology experts, developers, compounders, process engineers, and physicists. It offers a wealth of information for anyone interested in pursuing a career in this fascinating industry. Students of polymer chemistry and materials science looking for an elastic focus outside of thermoplastics will find this to be a complex and interesting subject. Finally, the book will provide inspiration and be a reliable resource for managers who care about improved product quality and reduced costs. The author would like to express his thanks to the German Rubber Institute that provide interesting contributions to the presented book. Without their firm backing and understanding, this effort could not have been accomplished.

Hanover, Germany *Robert H. Schuster*

November 2024

Contents

1 Introduction to Filled Elastomers

There is probably no industry more adept at using and varying raw materials than the rubber industry. In addition to the main components of each mixture – rubber, filler and plasticizer – the usual formulations contain a number of ingredients that have a certain functionality and interact with the main components. These include the ingredients that enable crosslinking to form a three-dimensional network or the anti-aging agents that are intended to reduce the rubber chains' susceptibility to oxygen. Assuming materials of satisfactory quality have been selected for the formulation, producing a high-quality mix represents the heart of the rubber processing. Subsequently the downstream processing and crosslinking to the end product are prerequisites for obtaining a high performance vulcanizate with the desired physical properties. With a few exceptions, the added fillers lead to a significant improvement in the rheological and, above all, the vulcanizate properties. In particular, the stress-strain behavior, the dynamic-mechanical properties and, above all, the fracture behavior, are significantly improved. The morphological features of the filler particles and the physical interaction with the rubber chain play a decisive role, and can effect significant improvements in the properties of the elastomers.

An elastomer is characterized by the crosslinking density of the rubber and the physical properties that result from the presence of a particulate filler and the oil added. Few elastomer applications can be envisaged without some level of reinforcing fillers. The effect of fillers on rubber reinforcement depends on the improvement of the properties, which depend on the primary particles, the shape of the filler aggregates, the loading, the aspect ratio of the aggregate, the interaction with the rubber chains and the chemical nature of the rubber. Four different types of filler have been developed for rubber technology that improve the physical properties of the elastomer due to their reinforcing properties:

- carbon black
- amorphous silica
- layered silicates
- carbon nanotubes

A characteristic of these types of fillers is that the particles are usually in the nanoscale when they are mixed into the rubber matrix. Nanocomposites are defined as composite materials characterized by the presence of dispersed filler particles whose size is in the nanoscale region, defined as having one or more dimensions in the order of 100 nm or less. Among these fillers, there are two groups which can be identified by the size of the particles and their shape. Carbon black and amorphous silica have a small aspect ratio, while layered silicates and especially multi-walled carbon nanotubes have a high specific surface area and a high aspect ratio. The first two fillers are incorporated into a rubber matrix in much higher concentrations, while the last two are used at low concentrations on account of their high aspect ratio.

Carbon black and precipitated silica are iso-dimensional fillers used in the production of filled elastomers. When properly dispersed in the rubber matrix, their particle size, aggregate structures and special surface properties make them unique among filled elastomers. The two-dimensional layered silicates and uni-dimensional multi-walled carbon nanotubes in particular are used, because their high aspect ratio and high specific surface area deliver physical improvements at small volume fractions.

Carbon black is the most important and the most used filler in the rubber industry. The generic term “carbon black” refers to a group of industrial products composed essentially of elemental carbon that is coalesced mainly into aggregates and agglomerates in an industrial manufacturing process. Their physical effects in natural rubber (NR) were published over 100 years ago. The first study on fillers in rubber was produced in 1891 [1] and true reinforcement was first reported in 1906 [2]. The discovery of the reinforcing effect of carbon black by S. Ch. Mote in 1904, who realized that the tensile strength and abrasion resistance of natural rubber are significantly improved by the addition of carbon black, opened the door for modern rubber compounds [3]. From that time on, carbon black been produced to improve the performance of rubber products manufactured from natural rubber (NR) initially and later from synthetic rubber (SR).

Carbon black is manufactured in different ways. The most common is thermo-oxidative decomposition of aromatic mineral oil. The second is the thermal decompositions of low hydrocarbons. The phenomenon of reinforcement remained defined and was only partially understood for the first few decades, due to the chemical and physical complexity of commercial important carbon blacks and the difficulty of measuring the complex mechanical properties. Reinforcement was defined as an increase in stiffness, modulus of elasticity, rupture energy, tensile strength, and resistance to cracking, fatigue and abrasion. Improvements were made to the specific surface area

and the geometry of the aggregates, as ascertained initially by determining the iodine adsorption and the tinting strength. Surface activity can promote better compatibility between the filler surface and the rubber chains, which improves the reinforcement of the rubber. The production technology was improved and the yield of the processes significantly increased. Contrary to pessimistic assumptions, the carbon black industry survived the oil crisis without major losses and continued to develop.

Modified carbon black types were created that exhibit much-improved morphology in the rubber compounds, and leads to a significant improvement in reinforcement. The so-called "magic triangle" which reduces rolling resistance, friction and grip, and abrasion resistance was improved by certain types of rubber. Although the same grade may be prepared by different manufacturers, it may not be identical in terms of processing or physical properties after the final curing step. Global production was 5 million metric tons per year but, due to its polluting nature, carbon black depends on petroleum feedstock for manufacturing. Nowadays, compounders can choose the right carbon back for a specific application from a wide range of grades available on the market. Carbon black is the most important rubber filler for tires, as it can increase the speed of cars and extend the tires' life time. More than 80 percent is used in the automotive market alone, with 20 percent finding use in non-automotive applications, such as printing inks and plastics. By 2022, the volume of carbon black was estimated to have risen to more than 15 million tons. In rubber compounds, they are used in a loading of 10–60 wt.% and offer an advantage in terms of physical properties. Carbon black manufacturers strive to produce products that meet the analytical and performance specifications for each grade, but owing the difference in the furnace geometry and the origin of the feedstock. In the second half of the 20th century, the reinforcing properties that carbon black imparts to rubber were the subject of a large number of books, of which a small selection can be found in [4–9].

Non-black fillers have always been an important part of the rubber industry. They represent the principal fillers originally used in rubber technology, which almost exclusively uses natural rubber (NR). The early non-black fillers were mainly naturally occurring minerals, such as clay, whiting, zinc oxide, calcium carbonate and others. But these non-black fillers merely diluted the amount of the rubber in the formulation and failed to produce any significant improvement in the performance of the vulcanized NR.

With the Second World War came the industrial production of amorphous silica. Fumed silica, which is obtained from $SiCl_4$ in a gas-phase reaction is less polar, but has silanol groups on its surface. Today, this material is mainly used to boost the physical properties of silicone rubber. Some years later, an aqueous solution of Na_2SiO_3 and H_2SO_4 was used to synthesize amorphous precipitated silica, which has a better quality than fumed silica and is particularly useful in polar rubber, such as acrylonitrile-butadiene rubber (NBR). In addition to carbon black, mention should be made of precipitated silicas, which is the second largest class for rubber applications todays.

These fillers contain a high proportion of silanol groups on their surface and exhibit strong filler-filler interactions. They are differentiated according to their activity, although the transitions between the different activity levels are fluid. Precipitated silica emerged in 1950, when amorphous silica demonstrated better reinforcing effects than fumed silica, but at a lower price [10–13]. Initially, precipitated silica was used for shoe soles and for off-road tire-tread compounds to improve chipping and chunking resistance. The reason for this discrepancy is the high polarity of precipitated silica which makes it less compatible with non-polar rubbers, such as NR and styrene-butadiene rubber (SBR). Up to 1970, precipitated silica was used for shoe soles and truck tires, where abrasion resistance was low. However, the great advance made in precipitated silica was the use of organo-silanes, which significantly reduced the polarity of the silica surface, enabling its use in unsaturated non-polar rubber. With the discovery of organo-silanes [10, 14], which can transform a polar surface into a non-polar surface, precipitated silica became a competitive material that provides non-polar rubber with a similar level of reinforcement as carbon black. This treatment renders the product less hydrophilic and produces a typical hydrophobic effect, where filler-filler interaction is at a low level. The initial concept was developed at Bridgestone [15] and commercially introduced by Michelin [16] with its “green tire” technology with a tire tread based on silanized silica in S-SBR/cis-BR blends that improves wet grip and rolling resistance. The high concentration of silanized precipitated silica poses special technological problems in achieving an excellent silica dispersion. Some silanized silica rubber treads must be mixed several times in an internal mixer to deliver a high tire quality. Global consumption is running at more than 1 million metric tons and growing significantly.

Layered silicates are hydrophilic fillers that cannot be dispersed in rubber compounds by a mechanical process, as the tactoids cannot be destroyed in an internal mixer and remain behind as hard agglomerates. Interest in layered silicates increased after 1990 when Toyota researchers used quaternary ammonium salts to produce organo-clays that widened the diameter of the layers and could be mixed with polar polymers [17]. It was found that tactoids can be intercalated and exfoliated by treating the suspension with quaternary ammonium salts and blending it with a polar polymer. Consequently, the high specific surface area and the high aspect ratio can be used to improve the physical properties of rubber [18, 19]. After transformation, the fillers were used in different types of polar rubber. Wet compounding proved to be the best method for using layered silicates without any transformation to improve the barrier properties of different polar polymers [20–22]. Layered silicates are environmentally-friendly fillers and pose no a risk to humans, as they occur naturally in pristine form in large quantities.

At the end of the last century, allotropic carbon forms were synthesized and have had an enormous impact on various applications. Carbon nanotubes have attracted the interest of academia and industry [23, 24]. A large number of reports have heightened interest in understanding the structure-property relationship and finding useful ap-

plications. Multi-walled carbon nanotubes are characterized by a high specific surface area and a high aspect ratio and exhibit remarkable mechanical and electrical properties that cannot be achieved with other fillers. The mechanical properties of carbon nanotubes in a rubber matrix makes them candidates for high reinforcement, due to their low density, high aspect ratio and high specific surface area. Rubber nanocomposites reinforced with carbon nanotubes can be considered a kind of particulate composite that varies extensively with the state of the dispersion and the alignment. Carbon nanotubes can be used in very low concentrations (less than 5 wt.%) on account of their high specific surface area and high aspect ratio. The effect of the fillers described is enhanced by the reinforcement they exert in the soft rubber and by the improvement in activity arising from the interaction with the rubber chains.

1.1 Reinforcement of Elastomers

An important property is the dispersion of the filler in the rubber matrix and the uniform distribution within it. This ensures good interaction between the filler and the rubber. The dispersion of the filler has always been an important factor for the quality of the rubber compound. Therefore, the mixing of the filler and the choice of mixing tool are predicated on achieving good dispersion at short mixing times. To an extent depending on the degree of dispersion achieved in the rubber compound, the physical properties of the elastomer are significantly improved. This reinforcing effect is described by the attachment of the rubber chains to the filler surface, which leads to reduced chain mobility and is characterized overall by a high level of reinforcement.

The term “rubber reinforcement” refers to the sum of the rubber-filler interactions in the interface between the filler surface and the rubber chains, especially in the cross-linked state of the rubber. The term “reinforcement” was introduced in 1920 by Wiegand, a pioneer in rubber science, who saw the effect of the filler as a particular contribution to significant increase in elastomer properties [25]. The importance of adequate surface bonding in filled rubber compounds was addressed by Wiegand, when he wrote in an article published in 1925: “… with a reinforcing pigment the surface energy is sufficient to prevent the tensional stress in the rubber phase from separating the rubber-pigment surface…”. This statement contains the essence of rubber-filler interaction and filler dispersion. It is on one hand the degree of filler dispersion, which indicates the reduced particle size, and on the other hand the bonding of the rubber chains to the filler surface, which converts this geometric requirement into an energetic factor, that enables the material to withstand large dynamic loads. The increase in fracture energy (integral of the stress-strain curve) was introduced as a criterion for the reinforcing effect of fillers. Comparison of the fracture energy of

different fillers reveals a steady decrease with increase in concentration of inactive fillers and an increase in the case of reinforcing fillers until the property reaches a maximum [26].

It is worth noting that the term “reinforcement” does not mean the enhancement of a specific physical property, but rather comprises the beneficial changes in elastomer properties generated by the use of active fillers. Thus, “reinforcement” is a technical-commercial value and not a defined property. Reinforcement is to be understood as the sum of the beneficial improvements conferred on the product by the presence of the filler, which should be well dispersed and homogenized in the elastomer [27]. It is ultimately the physical properties demonstrated to use the filler reinforcement. That will determine the composite utility, while its proliferation will be determined by the cost of the product. One can refer to the filled rubber materials as nanocomposites, even though this term was only introduced three decades ago, but the reinforcement of elastomers has been studied for many decades before that. Before the beneficial effects of the reinforcing fillers were known, naturally occurring minerals, such as clay, zinc oxide, mica and others that are above the nano size limit, were used to occupy space in the rubber compound and dilute the expensive natural rubber imported from Brazil and Southeast Asia. The fillers lowered the price of the natural rubber vulcanizate, but did not reinforce the filled rubbery material. If the development of reinforcements in rubber composites is considered in terms of the use of carbon black, parallels with car development can be seen, both in tire technology, where abrasion resistance and rolling resistance play a role, but also under the hood, where heat resistance, aging resistance and fuel transport play a role. In all other areas, filler-reinforced elastomers play an important role in our society, be it in bridge construction, earthquake protection or home comfort.

It was found that the physical properties of such nanocomposites exceed those of unfilled rubber vulcanizates many times over. The beneficial improvement in the use of carbon black as a nanoscale filler was recognized for synthetic rubbers, which show a significant tremendous increase in performance. Over the last century, it has become clear that carbon black as a filler can significantly enhance the property of rubber while lowering costs [5, 6]. Besides its environmental benefits, the manufacturing process allows for greater flexibility, as it is able to manufacture more different grades of carbon blacks in terms of quality, type and quantity.

In addition to the class of carbon blacks, significant improvements have resulted from the use of silanized silica in non-polar rubber, which in S-SBR/cis-BR effects a substantial improvement in wet grip and rolling resistance in automotive treads. More knowledge is also being gained in the use of fillers of high aspect ratio and high specific surface to improve reinforcement. The physical basics can be seen in the use of exfoliated layered silicates or isolated carbon nanotubes, which depend on the high aspect ratio and the increased specific surface area as well as the dispersion of the filler, and manage with a low concentration in the vulcanizate. Although the use of

carbon nanotubes leads to a high degree of reinforcement in rubber compounds, it also greatly affects the electrical conductivity needed in the rubber matrix.

One option that is being used more and more frequently is the use of hybrid fillers, i. e. the use of a large quantity of conventional fillers alongside a small quantity of carbon nanotubes or layered silicates.

1.2 Rubber Melts and Elastomers

To keep the terminology consistent, the term "rubber" will be reserved for the raw rubber obtained by polymerization reactions or by tapping the *Hevea brasiliensis* tree, while "elastomer" will be used for the Brasiliense's vulcanized rubber or elastic engineering material. The unfilled rubber melt is an assembly of polymer chains of small cross-sectional diameter that possesses a glass transition temperature below 0 °C, where the melt takes on a glassy consistency and can easily break. Above the glass transition temperature, the rubber melt can be deformed by an external force, but it will not return to its original dimensions when the force is removed, on account of the entanglement of the rubber chains and residual elongation in the rubber melt. The rubber melt is a quasi-elastic assembly arising from the entangled and elastic rubber chains. Due to the entanglements in the raw rubber melt, the material exhibits viscoelastic behavior; in other words, it behaves in between the deformation of an ideal solid and an ideal viscous material. The degree of viscoelasticity depends on the length of the rubber chain, the number of entanglements and finally the crosslinking density.

Chemical crosslinking causes the rubber melt to enter a vulcanized state that is characterized by a wide-meshed network, such that the large distance between the network nodes makes the crosslinked chains elastic. Such a vulcanizate is also known as an elastomer. When a force is applied to the elastomer, rapid deformation takes place and when the force is removed, the elastomer quickly returns to its original size. The difference between the behavior of the elastomer and that of the non-crosslinked rubber compound is shown in Figure 1.1.

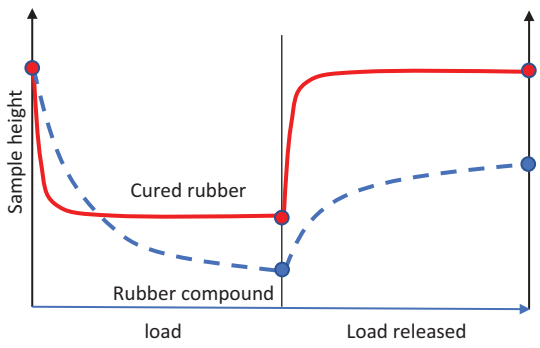

Figure 1.1
Response to a filler force acting on the mixed compound and the vulcanizate

Crosslinking of the rubber chains transforms the system from a free-flowing rubber melt into an elastic material, the elastomer. The chain sections between adjacent crosslinks are long enough to take on a coil-like shape and make the elastomer highly elastic.

The manufacture of elastic rubber chains is characterized by the polymerization reaction of monomers, i. e. olefins and dienes. During polymerization, the monomers are linked together to form long-chain macromolecules and, due to the low glass transition temperature, highly elastic rubber chains. The synthesis of rubbers uses different monomers to generate the polymerization mechanism [28–30]:

- radical mechanism
- anionic mechanism
- cationic mechanism
- coordination catalysis

The resulting rubber is divided into homo- and copolymers in accordance with the composition of the monomer. Copolymers use the properties of both monomers and therefore change the physical behavior. They can form linear or branched polymers, depending on the mechanism of polymerization. The macrostructure of the chain molecules has a significant influence on the processing behavior and crosslinking as well as the physical properties of the rubber. One exception is anionic polymerization, which yields linear polymers of different chain lengths and a narrow molecular weight distribution. The other strategies for polymerizing the monomers, lead to long-chain, branched polymers with a broad molar mass distribution. According to ISO 1629, the classification of rubber is based on the chemical structure shown in Table 1.1.

Table 1.1 Classification of Rubber

Chemical Composition	Rubber Grade	Type
Unsaturated chains (diene rubber)	NR, SBR, CR, NBR, IR und IIR	R
Saturated chains (polymethylene chain)	EPDM, EPM, CM, ACM	M
C-O bonds in the main chain	ECA, GPO	O
Silicone rubber	MQ, MVQ, MPVQ, MFQ	Q
Polyurethane rubber	AV, EV	U
Sulfur in the main chain	Polysulfide rubber	T

Finding the right choice of rubber, which is essential for reinforcement, can be an important task for a compounder, especially when mixing with appropriate fillers of a certain activity. The next task is chemical crosslinking, for which reliable chemicals are sought and in turn is another task for the compounder. Crosslinking of the unsaturated rubber is carried out with sulfur and accelerators or with peroxides at elevated temperatures, above 120 °C, in the case of saturated chains which cannot be vulcanized with sulfur. For saturated rubbers the peroxides or the resins are used. To an extent depending on the type of crosslinking, the elastomer acquires defined properties that determine its physical behavior.

1.3 Entropy Elasticity

When an ideal rubber network is extended by an external force, the network chains are elongated in the direction of the force vector and the entropy of the entire network decreases. When the force is released, the network quickly returns to its initial state of higher system disorder. The elasticity of a rubber network is thermodynamically based on the change in conformational entropy and is referred to as entropy elasticity or rubber elasticity [31]. This reversible process corresponds to a quantitative transformation of mechanical energy into a lower state of entropy. The principle of entropy elasticity is shown in Figure 1.2.

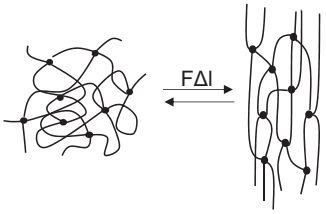

Figure 1.2
Concept behind entropy elasticity

The concept of entropy elasticity applies to ideally elastic bodies for which the theory does not provide for intra- and intermolecular interactions between the chains and internal friction processes of adjacent chains during deformation. The increased mechanical work is compensated for by a lower entropy of the polymer chains. For a system in thermodynamic equilibrium under isothermal conditions, the work done, W, is equal to the change in internal energy, U, and entropy, S:

$$dW = dU - TdS \tag{1.1}$$

where W is the work done, U is the internal energy, S is the entropy of the system and T is the absolute temperature

Assuming that the enthalpy does not change during deformation, the restoring force under strain increases with increase in temperature. This is known as the Joule effect:

$$f = -T\,(dS/dl) \tag{1.2}$$

where f is the restoring force, l is the length of deformation, S is the entropy, T is the absolute temperature

The calculation leads to an equation for an ideal unfilled elastomer that represents the applied mechanical energy as a reduction in the entropy of the elastic system:

$$F\Delta l = -T\Delta S \tag{1.3}$$

This relationship is describing the behavior of an ideal rubber network. For real networks, some corrections are needed that are related to the structure of the unfilled elastomer:

- presence of chain entanglement
- free chain ends
- inhomogeneities of the crosslinks
- different lengths of rubber chains

Generally, the equation describes the mechanical energy that is transformed into a higher-order network structure. Rapid deformation and recovery are important components of the elasticity of a rubber network.

Elastomers are soft and compressible materials with moduli of elasticity between 10^{-1} and 10^{2} MPa. They are characterized by high elongation of up to 1000%, behave hyper-elastically when deformed and have a positive temperature coefficient [32]. However, elastomers are limited in their application due to mechanical fracture failure. Fillers can significantly improve the physical properties and, especially, significantly reduce failure under extreme deformation [33]. Although real rubber networks deviate from this ideal state, this unique material concept is guides the behavior of both unfilled and filled elastomers. From a purely phenomenological point of view, elastomers differ from the other polymeric materials in four properties:

1. soft materials
2. highly elastic
3. dimensionally stable, and
4. small residual elongation after extensive elongation

In contrast, thermoplastic elastomers, which are crosslinked by physical interactions, are not crosslinked, but contain a hard phase and exist in a glassy or a semi-crystalline state. As opposed to this, elastomers exhibit highly elastic behavior from a temperature above of the glass transition temperature up to an elevated temperature at

which thermal decomposition of the rubber sets in. The residual elongation of elastomers is used to distinguish between elastomers, thermoplastic elastomers and thermoplastics. Elastomers have very low residual elongation (1–2%), while thermoplastic elastomers have much higher residual elongation (> 30%), with thermoplastic materials having the highest value, as shown in Figure 1.3.

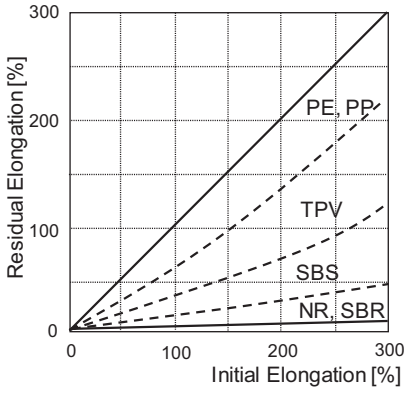

Figure 1.3
Residual elongations after stretching different classes of polymers

For any rubber network, the most important molecular characteristic is the crosslink density, which can be expressed either as the number of crosslinks or network chains per unit volume. The higher the crosslink density, the lower is the extensibility of the network chains and consequently the higher the force required to extend the network. Above a certain crosslink density, the entanglements are permanently locked or trapped between the network chains and contribute to the elastomer's resistance to uniaxial deformation. While the stiffness increases proportionally to the crosslink density and the hysteresis decreases inversely proportional to it, the ultimate properties, such as tensile strength and fatigue resistance show a characteristic maximum at a certain crosslink density that depends on network formation during vulcanization.

1.4 Advantages of Fillers

After the invention of vulcanization by Charles Goodyear (1839), the incorporation of a solid filler to dilute the expensive natural rubber became standard practice in rubber technology. The filler increases the viscosity of the filled rubber melt and the hardness is increased, the stress-strain behavior, the dynamic – mechanical moduli and the crack propagation is strongly reduced. The role of the filler in the interaction with the rubber chains is shown in Figure 1.4.

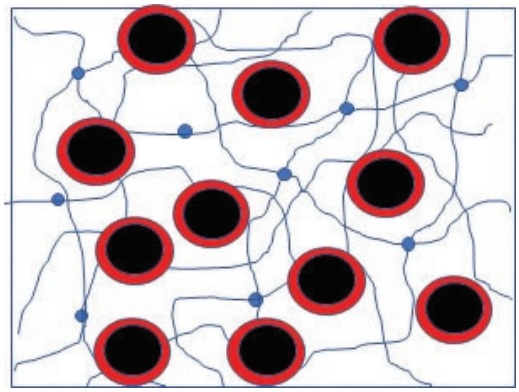

Figure 1.4
Filler in a rubber vulcanizate

Attempts were made to reduce the size of the particles to the filler aggregates, which are important for the physical properties of the elastomers. The incorporation of carbon black into the rubber compound and the subsequent dispersion of the aggregates reduces the fracture mechanical properties, such as tensile strength, tear energy and cut growth resistance and leads to a continuous improvement in the life time of the elastomer. The high-activity carbon blacks were used for the development of high-performance tire treads, while the semi-active carbon blacks were used for carcasses. In addition, a number of semi-active to active carbon blacks were used for technical rubber goods. Soon it was recognized that the dispersion of carbon black could be improved by providing better mixing elements for carbon black in the synthetic rubbers. Dispersion was an important challenge for the rubber industry if the performance of the rubber was to be improved. It can be assumed that dispersion is related to the interaction between the filler surface and the rubber material as the filler volume fraction increases (see Figure 1.4). The specific properties of the filled compounds change almost proportionally, such as the increase in tensile strength, the reduction in crack growth and the increase in tear energy [5–7]. The carbon blacks of highest surface activity are used comparatively little for tread compounds, because dispersion during mixing was not as good as for the grades of lower specific surface area.

1.5 The Role of Filler Activity

The degree to which the physical properties of an elastomer are increased by particulate fillers is qualified by the specific surface area, the “structure” of the filler aggregates and the filler activity. The term “activity” refers to the degree of interaction between rubber and filler during processing and in the vulcanized final state. Fillers of higher activity significantly increase the reinforcement of the elastomer. The activity range of the main groups of particulate fillers used in the rubber industry is shown in Figure 1.5.

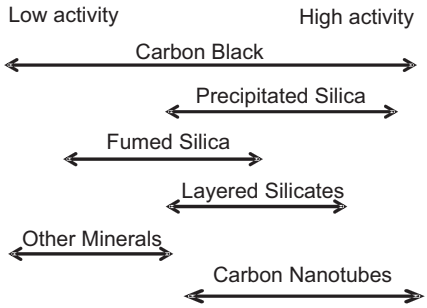

Figure 1.5
Activity of fillers used in rubber technology

The carbon blacks are produced under low reaction times to afford small primary particles that lower the price of the carbon black on account of the short residence time and low oil consumption. The carbon blacks are used in tread compounds and to enhance the vulcanizate properties and to increase abrasion resistance. The active fillers of high specific surface area yield reinforced elastomers that possess excellent physical properties, but are difficult to efficiently disperse. The activity of the fillers is associated with significant changes in rheological properties, such as an increase in the compound's viscosity and a reduction in extruder die swell. They provide major improvements in the physical properties of the rubber vulcanizate, especially enhancement of the ultimate properties, such as tensile strength, and a reduction in dynamic crack growth. The semi-active carbon blacks of larger primary particle size are produced at longer reaction times and are used at high loading capacity and are easy to disperse and process. Low-activity fillers result in less interaction between rubber and filler, allowing for better dispersion and downstream processing, which is reflected in extrusion or flexural strength, lower heat buildup, but their effect in terms of cut growth and abrasion resistance is rather limited. Carbon black imparts excellent flexural strength and good resilience to rubber and is preferred for mechanical goods, belts, hoses and cable jackets. As can be seen, carbon blacks cover the entire range from low to high activity and underline the importance in rubber technology and the wide range of technical applications in filled elastomers.

After suitable silanization, precipitated silicas exhibit medium to high activity, which improves dispersibility in non-polar rubber. Silanized silicas are now used in an increasing number of products, due to their good dispersibility, and ensure low rolling resistance and good wet grip of car tires, while interacting very well with the rubber chains. Fumed silicas are an active filler used for silicone rubber in medical applications.

Layered silicates can serve as pristine clays or can be transformed to organo-clay and are mainly used in polar rubbers that interact well with the two-dimensional platelets. They are important fillers that are aligned with the direction of flow and exhibit enhanced reinforcement in rubber components. Their main application in barrier properties demonstrates effective influence on the transport properties of gases and

liquids. They are important fillers for reducing the explosive decomposition of polar rubber compounds used in oil production.

Multi-walled carbon nanotubes exhibit a high activity in all rubbers at small volume fractions, mainly due to their exceptionally high specific surface area and high aspect ratio. Certainly, combination with iso-dimensional fillers lead to practical applications. Due to the high aspect ratio, multi-walled carbon nanotubes lead in combination with carbon black or precipitated silica to an improvement in important physical properties that cannot be achieved with a conventional filler. However, the price of carbon nanotubes is still prohibitive and their availability for broad industrial applications is far from satisfactory.

There is practically no physical property of elastomers that is not influenced to some extent by the interaction between rubber and filler and the affinity of the filler for rubber. Active fillers are able to build up strong physical interactions with polymer chains, which are adsorbed on the filler surface and form a dense polymer interface that causes physical phase adhesion. In contrast to this class of fillers, inactive fillers can only build up weak interactions with chain segments of the rubber and so rubber-filler phase adhesion is poor. The difference between an active and a non-active filler can be illustrated by the loading shown in Figure 1.6. In this illustration, it is assumed that the filler is actually completely dispersed in the rubber matrix. Active fillers increase the tensile strength and the abrasion resistance and pass through a maximum value when the filler loading is increased. This maximum value is characteristic of each type of carbon black in a rubber. After reaching the maximum, the ultimate properties decrease continuously to lower values.

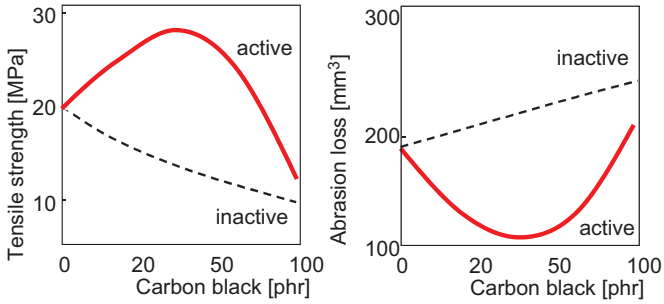

Figure 1.6 Effect of particle size on the enhancement of the mechanical properties

In the case of active carbon black, the property under consideration is improved up to loadings corresponding to a volume fraction of 0.17–0.19. However, the maximum values depend on the type of rubber and the activity of the filler as well as on the mixing conditions and the carbon black dispersion. However, the maximum values depend on the type of rubber and the activity of the filler as well as on the mixing conditions and the dispersion of the filler. Important vulcanizate properties, such as stress-strain

behavior, tensile strength, dynamic-mechanical properties, cut growth, abrasion resistance and tear resistance, are improved by active fillers, due to the presence of a rubbery interface layer that is physically bonded to the filler surface. In the case of semi-active carbon black, the tensile strength and abrasion resistance values decrease steadily as filler loading increases. It has been found that decreasing the particle size down to the nanoscale range boosts reinforcement of the mechanical properties according to an exponential function, as shown in Figure 1.7.

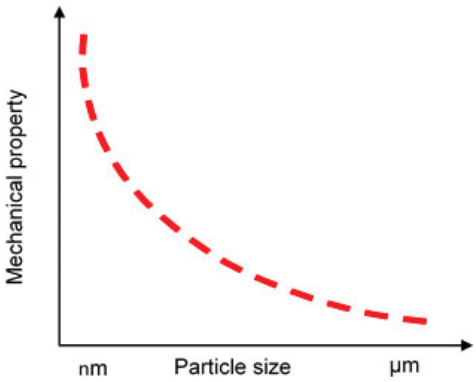

Figure 1.7
The properties of an elastomer increase with decrease in particle size

Since the fillers used in rubber technology are supplied by the suppliers in pelletized form, the filler particles have to be broken down during mixing in order to achieve reinforcement effects in elastomers. For this purpose, various internal mixer concepts with specific mixing rotors and cooling systems have been developed to improve dispersive and distributive mixing in the rubber compound at a certain temperature. While large particles disperse relatively quickly, fine particles can be difficult to disperse and may require more than one pass through the mixer. When the rubber compound is extruded through an extrusion die, it exhibits “elastic memory”. The fillers improve the extrusion properties by suppressing the elastic memory, and this ability to reduce swelling of the extrudate in the die is a direct function of the increased specific surface area and structure.

When using precipitated silica, hydrophobization of the polar silica surface with organo-silanes is required in order to achieve good dispersion in non-polar rubbers. Such treatment of the silica leads to low rolling resistance and excellent wet grip on tire treads. For layered silicates, it is important to use intercalated or, preferably, exfoliated layered silicates produced by wet compounding or organic clays to obtain good barrier properties. The use of carbon nanotubes is made possible by commercially oriented mixing processes, in which small volumes are incorporated into a rubber, mostly in combination with carbon black or silanized silica. In this way, the special effect of the high aspect ratio can be used to produce elastomers with very good strength, reduced dynamic crack growth and good abrasion resistance.

1.6 The Role of Filler Dispersion

The quality of elastomers containing reinforcing fillers depends not only on the physico-chemical properties of the rubber matrix, but also on the type and activity of the filler and dispersion of the filler during the mixing process. The dispersion of the filler is increased by the high elongational and shearing forces and the low mixing temperature. The greater the polymer-filler contact area and the interfacial interaction at the boundary of the rubber phases, the more bonding between the filler and the rubber leads to an improvement in dispersion. The key improvement is the progressive dispersion of the filler and the increase in beneficial contacts between the filler surface and the chemical chains of the rubber. Overall, the volume fraction of the rubber-filler interface providing the phase adhesion increases during dispersion and the proportion of non-dispersed filler agglomerates decrease. The fraction of non-dispersed filler leads to defects in the compound and premature failure of the vulcanizate, especially under continuous dynamic load. The effects of filler dispersion are shown in Figure 1.8.

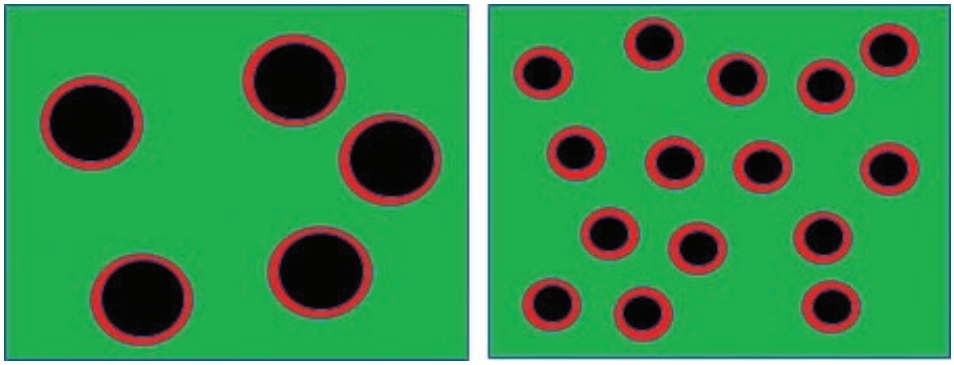

Figure 1.8 Dispersion increases the interaction between the filler surface and the rubber matrix

The bonding forces on the filler surface and the chemical nature of the rubber as well as the efficiency of the mixing tools contribute to better dispersion. The parameters of the mixing tool are largely responsible for good dispersion of the filler particles in the nanocomposite. It is important to know the degree of dispersion of the filler and the distribution of the filler during the mixing and downstream processes, as well as the influence of high temperatures during the induction time of the crosslinking process. It is advisable to routinely check the filler dispersion in the mixing chamber by means of user-friendly test methods and thus to derive the quality of the mixed rubber compound.

The effects arising from the dispersion of fillers must be understood as an interplay of material parameters that support the interaction between rubber and filler and the size reduction of particulate fillers. Thus, compounders should have a detailed knowledge of filler morphology and its role in the process of filler dispersion. This knowledge should exceed the level of commercial product specifications. In the author's opinion, it is important that compounders know in detail and are able to justify the choice of a particular type of filler and the loading used for the product.

The problem of selecting the right raw material for manufacturing a commercial elastomer falls to the compounder, who should be well versed not only in the performance of the raw rubbers, the type of fillers and the other ingredients of the formulation, but also in the multidisciplinary material science so as to be able to assess the multiple interactions and sometimes the conflicting interferences between the compound ingredients during mixing and downstream processing and final curing process curing to obtain the desired and specified properties of a competitive product.

The information about the particular functionalities of compound ingredients, their interactions in the compounds and in the vulcanizates or the interferences and interdependencies during mixing and further processing cannot be conveyed in sufficient detail to compounders, process engineers and experts active in research and development in companies that do not have access to specialist libraries.

That reinforcement is still at the center of research and that innovations are still being made in fillers and polymers are an indicator of its importance. In recent decades, the topic has gained much interest in connection with the development of high-performance elastomers and the more efficient use of raw materials, including the reduction of waste. The concepts developed for understanding the reinforcement of elastomers by particulate fillers consider the colloidal properties of the fillers, especially the specific surface area and the shape (or "structure") of the particles (i. e. aggregates) and assume an "ideal" dispersion, i. e. the size of the filler particles is reduced to the smallest level possible. However, an "ideal" dispersion is not achieved in real compounds manufactured on two-roll mills or internal mixers. A real, filled compound, even one used for a scientific study, contains particles whose size distribution is broad or narrow to an extent depending on the mixing technique employed. Thus, the particle size distribution in real compounds ranges from nanoparticles to pellet fragments.

As rubber manufacturers today are increasingly faced with economic pressures and rising demands on product quality and durability, it seems necessary to identify the potential of compound ingredients for transforming them into quality elastomers that meet the stringent requirements of the market. A look at the main components of rubber compounds – rubber, filler and plasticizer – reveals that they account for 90% of the total weight, but only 80% of product performance and 80% of product cost. The remaining 20% is covered by the vulcanization system and the antioxidants. Ownership of the rubber formulation makes it possible to control material cost at the

expense of running a materials development department and a mixing chamber [35]. Raw materials must therefore be used consciously in order that production efficiency may be maximized and waste minimized, as shown in Figure 1.9.

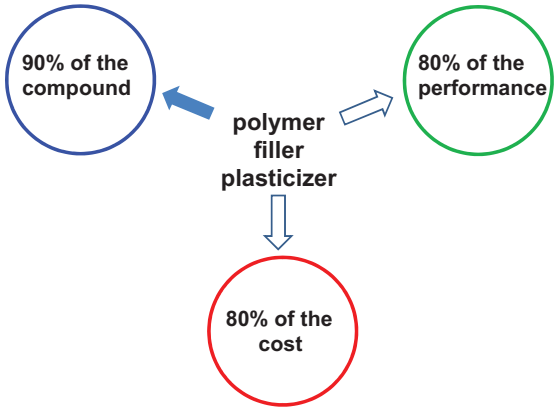

Figure 1.9
Importance of the main compounding ingredients

This requires the potential of all ingredients to be identified and fully exploited at a competitive cost. This task calls for complex knowledge of the functionality of each ingredient, the order in which they are added to the mixing tool, the mutual interactions of the ingredients during mixing, the degree of filler dispersion achieved during mixing, the changes that occur during extrusion, calendaring, shaping and molding and the curing state achieved during vulcanization.

As a side-effect, the better the knowledge of the material functionalities during processing and in the product, the less effort is needed to identify superfluous compound ingredients. In recipes still used in the rubber industry today, there are a number of ingredients that are intended to serve the same purpose or those that have no purpose. The elimination of such useless ingredients contributes substantially to the reduction of manufacturing costs.

In order to meet the requirements for an end product with specific properties, the compounder must select the rubber with the best performance. This requires a consistent knowledge of the property set of the rubber, its interaction with reinforcing fillers and the impact of the impact of the interaction on flow behavior of the compound, and finally the curing behavior. Any problem that arises because of an unsatisfactory property of the product or unsatisfactory processability requires a definitive answer on how to change the manufacturing process or to find a better formulation. The relationship between the formulation ingredients and the manufacturing process must be background knowledge for daily operations and problem solving.

The nature of the intimate mechanism is still not completely elucidated. More than 40 years ago Gerard Kraus wrote: “One might think that in such a mature field, most of the important questions would have been settled long ago. This is not so; few topics

in rubber science still continue to be the subject of more controversy. To understand why, one only needs to keep in mind the great complexity of the system" [36]. The complex behavior of a filled elastomer results from the different types of filler and rubber chains of specific elasticity. To an extent depending on the type of mixing, the internal mixer, the order of addition of the ingredients, the mixing temperatures, the mixing time and the geometry and speed of the rotors, the loading factor, the dispersion and distribution of the filler in the rubber can be increased. The morphology of the rubber compound is determined solely by the interfacial tension between the rubber and the filler during the mixing process. In addition, the plasticizers, the antioxidants and, above all, the crosslinking system contribute to the formation of the elastomer.

The rubber-filler influences determine the range of properties of the filled elastomers in extreme temperatures and make it possible to further improve their performance limit. Without filled elastomers, both comfort and strategic importance in the mobile world would be inconceivable. An understanding of filled elastomers is an important prerequisite for further improving their properties, especially through the use of conventional fillers and new nanofillers.

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2 Active Fillers

Developing an efficient formulation and finding the best conditions for flawless processing on the equipment available in the factory requires knowledge of raw materials and their interactions during processing. Compounding requires a thorough understanding of all raw materials and a deep knowledge of the functionality of the compound ingredients during processing. Considering that the reinforcement of elastomers provided by nanoscale fillers is based on the size and morphology of the fillers interacting with the rubber, it is appropriate to first introduce the manufacturing processes for the filler classes used in the rubber industry. As the origin of all reinforcement effects lies in the interaction of nanoscale fillers and the rubber chains, the formation of the filler particles is presented in this chapter. The technology for producing the filler particles is described in the following technical processes.

2.1 Carbon Black

Carbon black is the generally accepted term for the most important class of fillers for the rubber industry. Carbon black consists of elemental carbon aggregates, which are discussed in textbooks and relevant reports [1–4]. There are different types of carbon black covering a wide range of specific surface area and "structure" and exhibiting different activity in their interaction with rubber, ranging from low-activity to semi-reinforcing carbon blacks used in tire carcasses and rubber goods and high-activity carbon blacks mainly used in tire tread compounds. The manufacturing process is divided into two groups of technologies. The main group utilizes the incomplete or partial combustion of aromatic hydrocarbons. The chemical reaction for carbon black production by thermal-oxidative decomposition of hydrocarbons can be formulated as follows:

$$C_xH_y + O_2 \rightarrow \text{Carbon black} + CO + CO_2 + H_2 + H_2O$$

This process can be ensured by various methods and process parameters and leads to carbon black grades of different particle sizes, structures and surface activities. This group includes the furnace blacks, the gas blacks, the channel blacks and the lamp blacks, as mentioned in Table 2.1, which lists the different chemical processes, the manufacturing process and the feedstock that lead to carbon black. The most commonly used technology is the furnace black process, which is based on incomplete combustion of crude aromatic oil and tar oil products. Furnace production has a yield of 70% and covers the production of 95% the world's carbon black [2, 3].

The second technological process is the thermal decomposition of low molecular weight hydrocarbons in the absence of oxygen. This is called thermal black technology and it yields larger carbon black particles. The thermal decomposition process yields carbon black and hydrogen:

$$C_xH_y \rightarrow \text{Carbon black} + H_2$$

There are two processes for the thermal decomposition of hydrocarbons, which differ significantly both in terms of the feedstock and the properties of the resulting carbon black. Thermal blacks are obtained from natural gas and low-boiling oil hydrocarbons, while acetylene blacks are obtained from acetylene; both have a special morphology and in the case of acetylene black a high electrical conductivity. These thermal blacks account for up to 5% of global production [2]. A summary of the different methods used to produce carbon black along with the feedstock and global production is given in Table 2.1.

Table 2.1 Chemical Process (Types of Carbon Black and Feedstock Used)

Chemical Process	Manufacturing Process	Percentage of Production	Feedstock
Partial combustion	Furnace black	95%	Aromatic oils, coal tar oils Natural gas
	Gas black		Coal tar oils
	Channel black		Natural gas
	Lamp black		Petrochemical oils, coal tar oils
Thermal decomposition	Thermal black	5%	Natural gas, oil
	Acetylene black		Acetylene

The various carbon black processes were named for their industrial use. The first industrial carbon black produced was channel black, but after 1889 the furnace process was introduced, which guaranteed a higher yield and wide variety of specific surface areas [5].

2.1.1 Thermo-Oxidative Process

This process is based on the transformation of the aromatic feedstock, which decomposes at high temperatures to produce a carbon black that interacts well with the rubber. The main argument for using the thermo-oxidative process is to ensure economical production and to meet customer expectations regarding this wide variety of carbon black. However, the manufacturing companies need space for:

- storage of the oil feedstock
- the reaction for forming carbon black
- filtration/separation from the tail gas
- pelletizing, and
- drying and shipping

Today the technology has been refined to produce different carbon blacks with different specific surface areas and structures. However, carbon black has fundamental properties that cannot be obtained with other groups of fillers. In addition to being inexpensive and relatively easy to produce, they also offer a wide range of possible applications in rubber compounds.

2.1.1.1 Channel Black Process

The first carbon black process was the channel black, which was introduced in 1872 in Texas using natural gas from the oil industry [6]. The carbon source in the channel process is the natural gas from which the lower-boiling gasoline was used. The name channel black stems from the iron channels used to collect the carbon black deposited by small natural gas flames striking the surface of the channels. The channels are moved in a slow, reciprocating motion over stationary scrapers. The carbon black is collected in large containers and conveyed to packaging by a longer shift. The channel black process is shown in Figure 2.1.

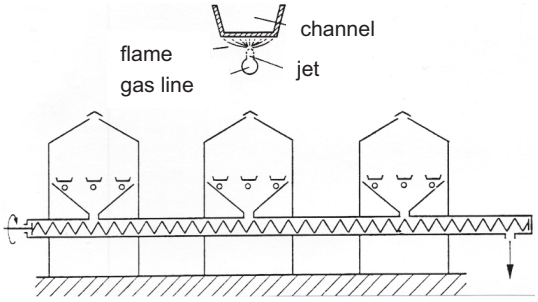

Figure 2.1
Channel black process

For most non-rubber applications, the carbon black is then packed into paper bags. For rubber applications, it is occasionally dry-pelletized in large horizontally rotating pelletizing drums. The process of channel black has improved over the decades, but it remains a very-low-yield process and has not been able to compete with the increase in market size in the tire industry. The oxidation causes the oxygen content of the carbon black to increase from 3% to as much as 10%, reducing the particle diameter from 30 nm to much lower values. The particle size of channel carbon black was rather small and the surface of the particles was oxidized, a fact affected the reinforcement of rubber compounds and especially slowed down vulcanization [7]. The acidic nature of channel blacks also contributes to delaying scorch time and the cross-linking process in the rapid vulcanization of NR. Up until the 1940s, channel black played a role as a filler in the rapidly developing tire industry, but, due to oxygen functionalization, the extent of vulcanization was very low and so it was replaced by the more efficient furnace black, which does not affect vulcanization isotherms. The limited yield of channel black (3–6%) and the environmental hazard posed by the emission of very fine carbon black particles into the environment were the reasons for terminating the process.

2.1.1.2 Furnace Black Process

The gas furnace process was introduced industrially on a large scale in 1920, when the yield of the channel process was too low and the environmental conditions were no longer sufficient to produce large quantities of reinforcing carbon black for the tire industry [8]. Production in a gas furnace yields large particle sizes, with diameters over 50 nm. Manufacturing of small carbon black particles is carried out by the oil-furnace process, which was developed in 1942 [9]. During production in gas furnaces, a diffusion flame is generated by burning part of the natural gas with added air.

The furnace reactors are designed to operate as trouble-free as possible over a long period of time and to support aggressive conditions with short reaction times. The wide variety of furnace blacks requires different reactor designed and sizes to cover the full range of carbon blacks. Reactors for high surface area carbon black used for

tire treads operate with small reaction times and large turbulence to ensure rapid mixing of the feedstock with the hot environment. For low surface area carbon black, the reactors are larger and operate at lower temperatures and longer reaction times.

The furnace process offers a high yield of carbon black (approx. 70%) and a wider production of different types of carbon blacks. Furnace blacks have almost forced the others types of carbon black processes out of the market. The most common type of carbon black is furnace black (> 95%), which is produced in a continuous furnace process. Chemically speaking, highly aromatic hydrocarbons of molecular weight of up to 500 g/mol fulfill the conditions for use as feedstock. In order that oils with a high aromatic content may be used, recourse is made petrochemical mineral oils produced during cracking or those resulting from the distillation of coal tar. Suitable oils are selected on the basis of their density, boiling behavior, viscosity and asphaltene content. In particular, polynuclear aromatics are very useful, while short side chains with many double bonds enhance the quality of the feedstock. Long paraffinic side chains are not useful in this process. In contrast to the channel process, the aromatic oil feedstock, which should contain as few sulfur compounds as possible, is introduced into a reactor heated by a flame to a high temperature and is burned incompletely. Ash and sulfur accumulate in the carbon black and must be avoided. In Europe, naphthalene and anthracene oils are economically viable and frequently serve as feedstocks; coal tar is also used. Reports on feedstocks for carbon black production have been published [10, 11].

A furnace reactor consists of a refractory lined tube arranged either in horizontally or vertically. A linear diameter is used for preparing the semi-reinforcing carbon blacks of lower specific surface area or larger primary particle size that are used for carcass blacks in tire manufacturing and for technical rubber goods. For the reinforcing carbon blacks of high specific surface, the reactors are used in either horizontal or vertical forms of different length, and may be rectangular or cylindrical. Many producers operate with smaller reactors in parallel to increase the production of carbon black. Air and natural gas are introduced to increase the temperature in the combustion zone either axially, radially or tangentially. The feedstock can be introduced either axially or radially into the high-velocity section of the furnace.

A special model is the biconcentric reactor, where, in the first half, the diameter decreases linearly and the residence time decreases with the square of the distance, while thereafter the diameter increases and the residence time increases. Inside the reactor, at high velocities of the feedstock and the carbon black that forms, erosion takes place at the edges and can contribute to contamination of the carbon black with some impurities. A reactor geometry consisting of two conical halves is schematically shown in Figure 2.2 [3].

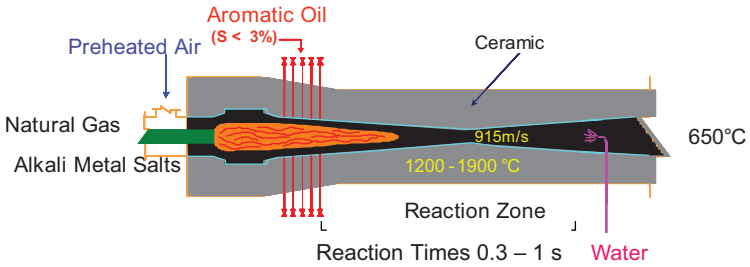

Figure 2.2 Biconcentric furnace for producing furnace carbon black. The alkali metal salts are introduced to obtain carbon black with reduced aggregate structure

The first zone of the reactor is the combustion zone in which the natural gas and air are completely combusted to generate the high temperature in the reactor. In the reaction zone, the gas flow is accelerated to higher velocities that allow the formation of irregular structured carbon black aggregates, resulting in intense to high velocities and turbulent mixing. Refinery heavy oil with a high fraction of aromatics, but with fewer sulfur compounds in the feedstock, ethylene cracker tar and coal tar distillates, which are produced during coke production, serve as the feedstock for the production of carbon blacks of smaller size. The hydrocarbon feedstock, generally preheated to about 250 °C, is injected into the end of the flame zone. The feedstock is atomized by introduction under pressure through specially designed nozzles. The turbulence required for the process is achieved via the chosen furnace design. The carbon black formed in the flame zone is fed through the furnace section at a high, pre-calculated speed. The heavy aromatic oils and tars give better yields than lighter oils with a higher fraction of hydrogen. At the high temperatures, the remaining oxygen is consumed by burning a small portion of the feedstock (less than 25–30%). Therefore, a portion of the feedstock is consumed in the reaction zone. If the temperature in the furnace is increased, a larger portion of the feedstock is burned and does not participate in the carbon black formation, a fact which increases the price of the fine furnace black.

The entropic nature of the furnace process determines the physical properties of the carbon black aggregates. The added feedstock is quickly decomposed and begins to dehydrogenate and form the carbon black in a turbulent process. In the reaction zone, the decisive portion of the feedstock, 70–75%, is very quickly converted into form carbon black aggregates in a reaction time of 0.3 to 1 s. The shorter the reaction time, the smaller is the primary particle size of the carbon black and the specific surface area and the higher the activity formed in the furnace process.

The hydrocarbon molecules are broken down into smaller units, which now form highly viscous aggregates in the turbulent atmosphere and simultaneously undergo dehydrogenation and carbonization, while the diameter of the primary particle increases during the reaction time. In a few fractions of a second, highly viscous droplet

aggregates are produced which carbonize in a very short time. The first section of the reactor comprises the combustion zone, where the fuel consisting of natural gas and an excess of process air is ignited to ensure a high temperature in the reactor. The combustion of natural gas generates the high temperatures in the furnace reactor that are required for thermally oxidative cracking of the oil feedstock. The temperatures reached are crucial for the type of carbon black to be produced. Depending on the primary particle size, temperatures of 1400 to 1900 °C are used.

For active carbon blacks that have a small primary particle size, a very short reaction time is chosen, while, for larger primary particles, these times are much higher. Consequently, a higher temperature of 1600 to 1800 °C is achieved by using more feedstock, but it leads to a smaller amount of carbon black and higher production costs. If less active carbon black is to be produced, for instance carcass carbon black, the temperature in the furnace reactor is kept lower, at around 1300–1400 °C, and that reduces the price of carbon black.

Reaction times vary with the choice of natural gas and air for the flame and the quantity of oil feedstock. The reaction times range from 0.3 s to 1 s before dehydrogenation is complete at the end of the reactor. With a suitable reactor design and a good oil/air ratio and a good residence time in the reactor zone, the particle size is distributed over a fairly wide range, as shown in Table 2.2.

Table 2.2 Particle Size and Reaction Time in the Reactor [12]

Carbon Black	Particle Size (nm)	Spec. Surface (m^2/g)	Speed (m/s)	Residence Time (s)
N 220	20	125	200–400	0.01
N 550	35	80	30–40	1
N 762	65	40	0.5–1.5	2

With increase in the residence time or reduction in the speed of the decomposing hydrocarbon, there is an increase in the particle diameter of the primary particles. Another representation combines the oil flow rate at constant fuel and air flow rates with the reaction temperature and the particle size of the final carbon black and is given in Table 2.3 [13]. This shows the relationship between the oil rate (kg/h) and the primary particle size at different set temperatures. If the oil rate decreases by half and the reaction temperature increases at the same time, the radius of the primary particles decreases by half. This is certainly associated with higher oil consumption. The particle size is primarily controlled by the feedstock rates and the temperature in the reactor. A higher combustion ratio increases the temperature in the furnace and reduce the particle size as well as the yield.

Table 2.3 Influence of Oil Rate at Constant Fuel and Air Rates on the Primary Particle Size [13]

Oil Rate (kg/h)	Reaction Temperature (°C)	Primary Particle Size (nm)
4060	1450	44
3660	1500	35
3170	1570	26
2740	1630	21
2370	1680	19

In order to reduce the "structure" of the carbon black aggregates, it was discovered that alkali metal salts additives can reduce the "structure" of the aggregates of carbon black. The positive charge of the potassium ions prevents the attachment of other charged aggregates and thus the number of primary particles in an aggregate can be increased. The alkali cations reduce the degree of aggregation in the reaction zone and produce carbon black with a smaller "structure" [14]. This may be done in the form of aqueous salt solutions injected directly into the furnace or through the use of an oil-soluble alkali metal compound [15]. Quantities of 5–25 ppm potassium chloride are used to significantly reduce the particle "structure". However, the process is also characterized by the geometry of the furnace and other inexactly given factors, which tend to make quality control difficult. High "structure" blacks, characterized by a high proportion of particles that clump together to form persistent aggregates are advantageously produced by controlling the turbulence of the decomposing feedstock in a desired pattern [16]. The particle size of the produced carbon black depends largely on the combustion ratio, i. e. the ratio of the total air present to air needed for the complete combustion of all hydrocarbons present. A high combustion ratio increases the flame temperature and reduces the particle size as well as the yield of the carbon black formed. The average diameter of the carbon black made by the furnace process varies from 85 nm for low specific area to 15–18 nm for high-activity carbon black. After the carbon black has formed in the reaction zone, it must be quenched by injecting water at a distance dependent on the type of carbon black to be produced. If the reaction time is shortened, a large quantity of water is required. The temperature of the product stream of the carbon black process is lowered to 650 °C, which also prevents any undesirable secondary reactions which reduce the yield of carbon black production.

The wet slurry is transported for filtration and separation of the carbon black and tail gas (mainly H_2 and small amounts of CO, CO_2, and N_2). Separation is done using commercial filter bags. The collected carbon black is removed from the filter bag, usually into a pneumatic conveying system that transports the carbon black until a secondary filter separates the gas. The gases produced during the reaction are combustible and,

in most cases, are fed into an afterburning stage where the heat is used to dry the carbon black, or are burnt in a boiler to generate steam. Since the filtered gas contains 30–50% water vapor, most filters are operated at elevated temperatures to avoid condensation. Two different types of backwash filter are used, namely repress back filters and pulse-jet filters. The filter bags are usually made of special surface-treated glass fibers and function for up to two years; afterwards, the filter has to be changed. The heat from the vapor stream is used to preheat the feedstock and air and to generate steam that can be used within the company or is discharged externally.

The separated carbon black consists of a mixture of loose aggregates and agglomerates with a very low apparent density of 20–60 g/l. This mixture is called "fluffy black" and must be compacted for handling. The fluffy black is densified by a pelletizing process or densified to facilitate onward handling. For the pelletization, two different technologies have been developed. The most commonly used is wet-pelletization, which has been employed industrially since 1922. It consists in mixing equal weight ratios of water and fluffy black in pin mixers. To promote the formation of easily dispersible pellets and to minimize the presence of undesirable fines, molasses from sugar refining or lignosulfonic salts, byproducts of paper manufacturing, are used. The liquid content of the charge has a profound effect on the rate of pellet growth [17]. The wet-pelletization process yields a pellet size of 1–2 mm that contains 50% of water and must then be dried. The wet-pelletizing process is commonly employed with all types of furnace carbon to form a user-friendly product [7, 18, 19]. The bulk density of the pelletized carbon black is 350 g/l. The wet-pelletizing process affords a technically and economically favorable process for the production of carbon black modifications. The size distribution of the pelletized carbon black is important for its behavior in automated transportation. The formation and quality of the pellets are dependent on the pelletizing speeds and the feed rates of carbon black and water. The pelletizing increases the bulk density for easy handling.

The second technology is dry-pelletization, in which the fluffy black is pelletized in inclined drums in the presence of an already pelletized material (seed) [19, 21]. Dry-pelletization is a simple, energy-saving process that produces softer pellets of smaller diameter. Special carbon blacks produced by the furnace black process are either loosely compacted and packaged as powder carbon blacks or converted into easily dispersible pellets by the dry-pelletizing process. Such carbon blacks are used to reinforce polyolefins, such as PE and PP.

The pelletized carbon black is dried in rotating gas-fired dryers. The water content must be reduced from the initial 50% to less than 1% before the product is delivered to the customer. Finally, the furnace black is passed over magnetic separators to remove metallic impurities. The carbon black compounds contain small amounts of solid impurities, such as coke particles, extraneous particles, and mostly grit, which is discharged via the grit separators.

The energy consumption in the production of one kilogram of furnace black is in the range of 9–16 × 10^7 J and the yields are 300–600 kg/m^3, the exact figure depending on the type of carbon black. Furnace black has a variable surface area of 25 to 145 m^2/g and a wide variety of structures. The pellets are fed into rotating gas-fired dryer and dried in an air stream at a temperature of 200 °C. The material is screened to remove material of an undesirable size and is transported to the shipping container.

The carbon black pellets must be able to withstand transportation, storage in silos and pneumatic conveying into the internal mixers. On the other hand, they must be soft enough to be easily crushed and dispersed during mixing. The complex manufacturing technology is shown schematically in Figure 2.3.

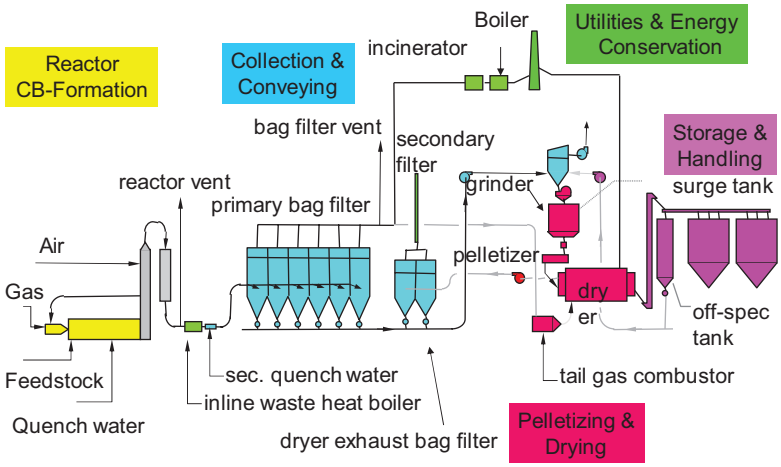

Figure 2.3 View of a furnace carbon black plant

After the production of carbon black, there are several necessary installations that prepare it for shipment to the customer. Carbon black can vary enormously in specific surface area and structure, and its surface activity, as a result of a functionalization process, ranges from low to very high values. It is produced in a very capital intensive and energy intensive process, making it inherently imperative to reduce energy costs throughout the production process. Therefore, in the furnace process the furnace blacks of varying particle size are shown in Figure 2.4 [27].

In addition, many different specific surfaces and structures of the filler aggregates can be achieved with furnace carbon black process. This method of production is expressly endorsed. The type of carbon black chosen for a given compound can greatly influence the properties of the compound, and also a major impact on the methods used to process the compound. With the development of emulsion SBR, the furnace carbon black demonstrates a similarly high reinforcement as the NR/carbon black vulcanizates.

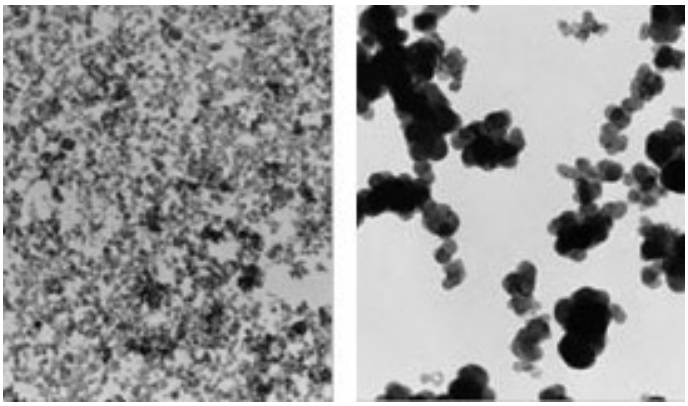

Figure 2.4 Aspects of furnace carbon blacks

2.1.1.3 Formation of Furnace Carbon Black

One of the most interesting aspects of the manufacture of carbon black is the mechanism by which it forms in the furnace reactor. Due to the high rate of carbon black formation, it is difficult to establish a simple correlation with what is happening in the reactor. However, many studies have unraveled the mechanism to some extent. It is beyond the scope of this treatise to review all reports, but the authors conclude that there are two distinct processes:

1. nucleation of the carbon particle, and
2. subsequent growth that leads to the aggregates

During the oxidative decomposition of hydrocarbons, it can be assumed that oxygen diffuses in the gaseous hydrocarbon stream and leads to formation of carbon black, namely the aggregates containing primary particles. This process was studied during the last century, but is not completely understood. No single mechanism can explain the formation from different feedstocks and different processes or how some is also produced on the walls of the reactor [23]. Some of the studies of the mechanism of nucleation and particle growth show that there are two phases in the formation of carbon black [24–26]. It is assumed that carbon black occurs in several stages in its formation [27]. It is also assumed that the condensation of degraded feedstock leads to small C_2 radicals that can form polyacetylene, which is not the only precursor for the forming carbon black [28]. The intermediate products are unsaturated and it appears that the formation of carbon black entails a polymerization process. Initially, liquid, highly viscous droplets are formed by polymerization of the unsaturated molecules. This hypothesis is consistent with the results on nucleation and growth of viscous particles [29–32].

At the beginning of the process, the feedstock is introduced as a gas or in finely dispersed form into the reaction zone at high temperature, initially forming C_2 and

C_2H_2 radicals, which then form polycyclic aromatics having a molar mass of 150 to 600 g/mol. Theories have been proposed which, on one hand, assume growth of free radicals on condensation nuclei [29, 33] or condensation of gaseous hydrocarbons and the continuing dehydrogenation leads to liquid droplets with high viscosity from which the solid particles are finally formed [34–38]. If the saturation limit is exceeded, they condense into droplets of small diameter (2–5 nm). As a result, further radicals and polycyclic hydrocarbons accumulate in the turbulent system of the reactor zone. Progressive dehydrogenation and growth of the polycyclic layers lead to an increase in droplet viscosity, so that on further collisions the droplets adhere to one another and form fused aggregates. Due to the progressive dehydrogenation of the particles, the viscosity increases and the polycyclic hydrocarbons are carbonized and form imperfect graphitic layers at the surface of the particles. Aggregates are formed which take on a solid form after a reaction time in which the dehydrogenation process occurs. The final solids are carbon black aggregates that flocculate to build larger agglomerates, due to van der Waals forces. As dehydrogenation of the particles and carbonization progress, the aggregates are formed through ballistic collision of the particles. Besides aggregate growth, resulting from the collision of neighboring aggregates, surface growth occurs due to the deposition of carbon atoms on the aggregate during the formation of primary carbon black aggregates according to an ordering principle that allow the superior graphitic layers to be more organized than those from the middle of the primary particles. [39–43].

On the basis of transmission electron micrographs, the concept of concentration seems to prevail when the final shape of the particles is considered. All carbon blacks have some formation features in common [44]:

- The particles generated at high temperature are generated in a supersaturated vapor phase and have a related micro-structure the micro-structure does not depend on the aggregate state of the feedstock, and
- the carbon black particles are formed from graphitic layers that are built into the particle according to an ordering principle.

The resonance-stabilized aromatic compounds arrange themselves, following the lowest energy in the sp^2 hybridization, in layers that are preferably oriented parallel with the surfaces of the droplets. Impurities, ions, and hydrocarbon molecules of high molar mass serve as nuclei. As aromatization progresses by dehydrogenation and carbonization, the agglomerated droplets become less and less likely to break apart, and a transition to a solid carbonized phase takes place. This means that the growth in size of the carbon aggregates is as good as complete [45]. The nucleation and growth mechanism demonstrate that the growth of the particle increases in very short reaction times. The formation of the droplets leads to a rapid decrease in vapor pressure, such that no formation of additional nuclei takes place. The growth of the particles continues on the existing nuclei. The continuity of the planar carbon microstructure in fused carbon black aggregates also indicates coalescence of the liquid droplets

prior to carbonization into solid carbon black aggregates. It has been shown that the temperatures required for growth of the aggregates are lower than those needed for nucleation of the carbon black particles. The various stages of formation of the carbon black aggregate are summarized in Table 2.4.

Table 2.4 Formation Components of the Carbon Black Aggregate [46]

Structural Unit	Time (ms)	Particle (nm)	Molar Mass (g/mol)
Organic radicals	< 0.5	-	25–50
Polycyclic aromatics	0.5–3.0	1–2	150–600
Cond. of aromatics	3–5	2–5	2400–40,000
Growth of particles	5–10	10–20	$> 10^5$
Aggregates	> 10	> 20	$> 10^6$

The aggregates formed in this way accumulate under van der Waals forces to form large agglomerates, which form what is referred to as "fluffy" carbon black. The fast and complicated process can be represented schematically by a simple model that shows disintegration of the feedstock into molecular fragments and the formation of viscous droplets, which subsequently split off hydrogen and undergo a process of carbonization to form the furnace carbon black aggregates. This is shown in Figure 2.5.

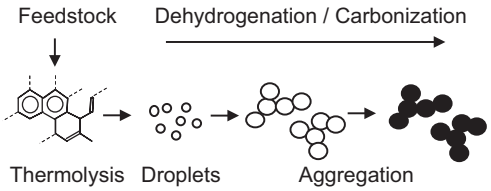

Figure 2.5
Mechanism behind furnace carbon black formation by dehydrogenation and carbonization of the mineral oil

Such aggregated particles subsequently end up agglomerating, producing what is known as fluffy carbon black. The fluffy black is free-flowing pellets of 0.3–1 mm in diameter that are difficult to handle in industry. The particle sizes and the shape of aggregates can be controlled by changing the processing parameters, such as feedstock flow rate, gas rate, air rate, air-to-gas ratio, quenching position and furnace geometry. The biconical reactor geometry allows a quadratic increase in the flow rate in the first section of the reactor and a decrease after the smallest part of the reactor. In this way, the residence time for the formation of the carbon black particles is shortened, while the time available for cooling the hot material is extended.

In addition to the influence of geometric parameters, the usual technique for adjusting the primary particle size of carbon blacks is to change the ratio of air to natural gas. An increase in the air-to-gas ratio leads to an increase in both the temperature

and the overall flow rate, which has a strong influence on the size of the carbon black aggregates. If this time is shortened, particle growth is reduced and the size of the primary particles is small (15–20 nm). If growth of the particle has more time to increase the size of the primary particle, the aggregate size also increases. According to some publications, the increase in the particle diameter is proportional to the residence time in the reactor [47].

$$\Delta d = c\, d\Delta t \tag{2.1}$$

where c is a constant, d is the size of the primary particle and t is the residence time in the reactor.

Integration of this equation leads to an exponential increase in the size of the primary particle with residence time in the reactor. The nuclei generally have a normal size distribution; particles formed at lower feedstock concentrations without significant growth should have a normal size distribution. It is not possible for carbon black aggregates consisting of coalesced nuclei to change to the normal particle size distribution. The higher the reactor temperature, the smaller the primary particle size becomes. As shown in Figure 2.6, increasing the furnace temperature leads to a substantial reduction in primary particle and aggregate size [1].

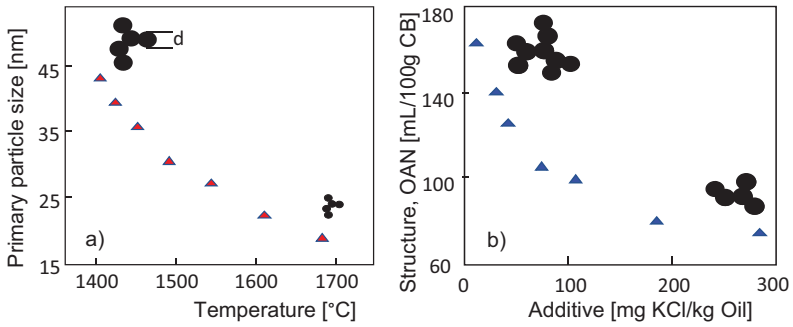

Figure 2.6 Morphology of primary particle formation: a) change in aggregate size with temperature and b) reduction in aggregate structure through incorporating potassium salt

Increasing the temperature in the reaction zone leads to a reduction in the diameter of the primary particles. Therefore, the average size of the primary carbon black particles can be adjusted via the process parameters. Ballistic collisions of carbonizing droplets in the turbulent flow prevailing in the reaction zone lead to the formation of branched aggregates. It is assumed that the irregular shape of the aggregates, the so-called "structure," is more dependent on the turbulence at the feedstock injection point. In order to reduce the degree of branching during the formation of the aggregates, a solution of potassium chloride is injected into the furnace. The positive ions

act as nucleation centers for the nanodroplets formed in the first stages of the process. Due to electrostatic repulsion between the similarly charged droplets, aggregation is largely prevented [48]. The reduction in the degree of branching triggered by the potassium salt is shown in Figure 2.6b. The presence of potassium cations reduced the predilection to form larger aggregates and the increase in structure is reduced to a lower level that can be measured experimentally.

The yield of furnace black depends on the feedstock used and the reactor temperature. Aromatic oils, which consist of polynuclear, unsubstituted aromatics, give rise to a higher yield. The primary particle sizes and the structure of carbon black can be controlled independently of each other, such that there are carbon blacks with increasing particle size, but the same aggregate branching and the case where the particle size is constant, but the aggregates have a different shape. Product quality is therefore determined by the process control, in which a large number of parameters must be taken into account, but are not changed frequently.

2.1.1.4 Gas Black Process

A further development of the channel process was operated by Degussa in Germany in 1930s, whereby the feedstock is obtained from tar distillation and hydrogen or air serves as a carrier gas on small flames under rotating drums that are cooled [2]. Gas black production is an open process with a constant air flow. The feedstock ranges widely from gases to renewable sources to highly aromatic oils, such as coal tar distillate or bottoms from the cracking process of naphthene oils for constant high quality products. The gas black apparatus consists of a burner pipe approximately 5 m long, which is fitted with 30–50 diffusion burners. The flames impinge on the surface of a water-cooled drum, where about half of the carbon black is deposited. The carrier gas is used to generate the energy required for the thermal decomposition of the hydrocarbon. The carbon black is continuously scraped off and transported to a filter system and deposited to be shifted to the rubber industry. Onward processing is then similar to the furnace black process. The gas black is collected in a sealed filter system that exceeds official emission standards by a significant margin.

Due to the continuous contact with oxygen in the flame and the decreasing temperature, the gas black process has special properties on the size of the primary particles and the size of the aggregates. The gas black is characterized by a loose structure and very good dispersibility in rubber compounds and plastics. The production rate is 7–9 kg/h and the observed yield is approx. 60%. The gas-phase process allows the production of a small primary particle size of 10–30 nm. A schematic representation of this technology is shown in Figure 2.7.

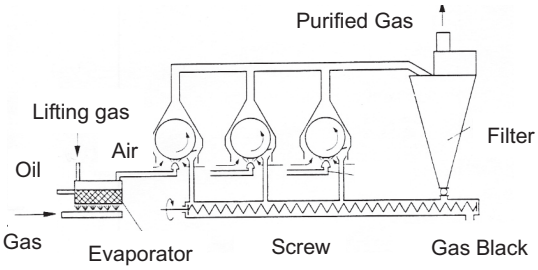

Figure 2.7
Scheme of the gas black process

The average primary particle diameter is 10–30 nm and the specific surface area are approx. 100 m^2/g. Gas blacks are characterized by their loose structure and good dispersibility. As a result of contact with oxygen at high temperatures, acidic functionalities are formed that can react with polar rubbers (i. e. NBR). As a result of contact with oxygen at high temperatures, acidic oxides are formed on the surface. Carbon black produced by this technology has small primary particles in the lower to medium particle size range and is used in rubber compounding, but also in in the paint industry. Oxidative post-treatment using nitrogen dioxide, ozone or other oxidants makes it possible to NBC further increase the acidic function for use in inks and coatings production.

2.1.1.5 Lamp Black Process

The lamp black process is the oldest and most primitive method of producing carbon black, but it is still used today. This type of carbon black is made by burning aromatic oils in shallow, open pans in a restricted area with a limited air supply. The process falls into the category of thermal-oxidative decomposition of the oil feedstock. The difference is that the temperature is relatively low and the temperature distribution is relatively large. The feedstock, oil with a high aromatic hydrocarbon content, is burned in shallow iron pans (diameter 1.5 m), which is surmounted by a fire-proofed flue hood that is lined with refractory bricks. The air gap between the pan and the hood, as well as the vacuum present in the system, help to regulate the air supply and thus to tune the carbon black's properties. The smoke from the burning pans passes though the ceramic chamber. The off-gas containing carbon black is sucked into an exhaust pipe, which is coated with a ceramic inner liner and leads to the cooling and collecting system. The smoke from the burning pans passes through low velocity settling chambers at the end of the simple reactor, from which the carbon black is cleaned by motor-driven plows. By varying the size of the burner pans and the amount of combustion air, the particle size can be controlled within relatively narrow limits, but the particle size is always significantly higher than in the furnace process. The carbon black resulting from the incomplete and slow combustion is then separated in chambers or cyclones [7]. The lamp black process is shown in Figure 2.8.

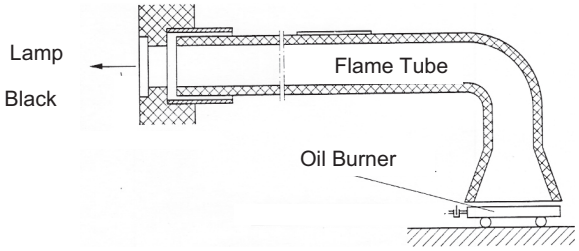

Figure 2.8 Lamp black process

Onward processing of lamp black is similar to that of the furnace blacks. A lamp black process can produce 100 kg/h of carbon black, because the oil burns slowly. Lamp carbon black has an average primary particle diameter greater than 65 nm, a specific surface area of 22 m^2/g and an aggregate structure of 130 mL/100 g.

Unlike the furnace carbon black process, the lamp black process does not allow any major changes in primary particle size, surface area and structure. In the past, different types of lamp black were produced. Typically lamp carbon black shows a very broad particle size distribution ranging from approx. 60 to 200 nm.

A more extensive description of the process and the properties of lamp carbon black can be found in the literature [1, 2]. Nevertheless, the typical lamp black process leaves a unique fingerprint of carbon black properties. It yields large quasi-spherical carbon black particles that have large particle size and small specific surface area and wide particle size distribution. This carbon black has a very low activity and is used to increase the hardness in EPDM or FKM and for special applications, where increasing the rubber properties is not as important as for active carbon blacks. Thermal blacks have good extrusion behavior and ensure a smooth extrudate surface.

2.1.2 Thermal Decomposition Process

Special carbon blacks are made by thermal decomposition, without using any oxygen in the process. Depending on the hydrocarbon used and the manufacturing technology one can use two types of carbon black manufacturing:

- thermal black process
- acetylene black process

In both cases, high temperatures are set in the process of forming carbon black at which the feedstock thermally decomposes into carbon black and hydrogen at 1000–1300 °C. Thermal black processes produce the carbon black from natural gas and the acetylene process use the exothermic decomposition of acetylene.

2.1.2.1 Thermal Black Process

At the beginning of the 20th century this process was used to produce hydrogen, but later the emphasis was placed on the production of a semi-active carbon black [1, 2]. This thermal carbon black is made by thermal decomposition of natural gas or low boiling liquid hydrocarbons in the absence of oxygen. The thermal black process is carried out at relatively low temperatures (about 1300 °C) and requires longer residence times than does the furnace process. The process is carried out in two cylindrical furnaces lined with an open checker-work of silica brick. While the first generator is heated with a stoichiometric mixture of the gaseous fuel and air, the second hot generator is charged with natural gas. Thermal decomposition takes place and about half of the carbon black is formed is swept out with the gases, while the rest remains on the bricks. After 4 to 5 minutes, natural gas is turned off and air and fuel are introduced for reheating the generator, first burning off the carbon remaining from the previous cycle. Since the reaction is endothermic, the temperature decreases and at 900 °C a new heating process starts. The material stream is finally quenched with water and filtered in a bag house. The distinction from other processes is that, in the thermal black process, energy generation and decomposition of the feedstock are not simultaneous. The fact that the carbon black produced occurs in the absence of oxygen and at decreasing temperatures, results in large carbon black particles with a wide agglomerate distribution. The existing carbon black may be further processed and pelletized, screened and packaged for shipment to customers. The process for producing thermal black is shown in Figure 2.9.

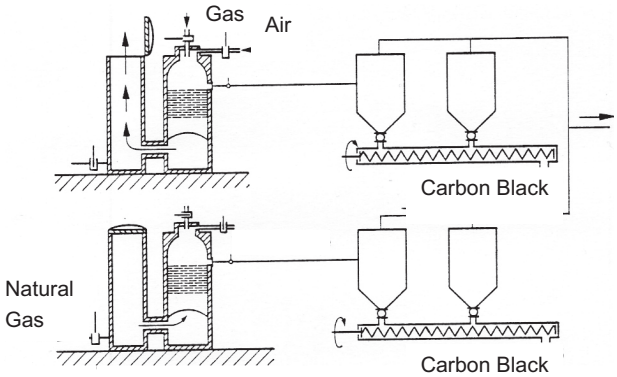

Figure 2.9 Thermal black process

Due to the long residence time at elevated temperatures, thermal blacks consist of nearly spherical particles that demonstrate a broad particle size distribution, the largest form of industrial carbon blacks. Thermal blacks form relatively slowly and yield coarse primary particles ranging from 300 to 500 nm. These carbon blacks have the lowest reinforcement of all carbon blacks.

The fraction of the smaller particles (approx. 0.5 µm average diameter) can reinforce moderately amorphous elastomers. However, since thermal blacks have a wide particle size distribution, their largest particles approach the limit of non-reinforcement. If the feedstock is only natural gas, it is possible to reduce the particle size to 120–200 nm, in which case it is called fine thermal black.

Medium thermal blacks (MT blacks) with a larger particle size of 300–500 nm are still produced by using an undiluted feedstock and the yield of MT blacks is 40%. Fine thermal blacks have diameter of 120–150 nm. Diluting the natural gas with hydrogen leads to a decrease in particle size. These carbon blacks are characterized by a high tar content (> 1%). The production and the properties of thermal black are described in several publications [7, 49]. Thermal carbon blacks are much more expensive than furnace carbon blacks due to their high energy requirements. Thermal carbon blacks have very good processing properties, but a low reinforcing effect and produce vulcanizates with low hardness, low compression set and low hysteresis. They can be used at high loadings to give benefits in some compounding applications. They have a high loading capacity and are used in mechanical goods, particularly in insulation jackets, as the electrical conductivity is relatively low. This type of carbon black is used in O-rings and seals due to its low hardness, high extensibility and low compression set, and low dynamic hysteresis. Thermal carbon blacks are employed as fillers for special rubbers such as FKM, CO, ECO, CSM.

2.1.2.2 Acetylen Black Process

Acetylene blacks are a special group produced by thermal decomposition of acetylene at high temperatures in a continuous process. In principle, there are two methods for producing acetylene black. The older method is based on the decomposition of compressed acetylene in steel pressure vessels, initiated by an electrical discharge [50]. The process used today works at normal pressure and is based on the thermal decomposition of acetylene in a preheated reactor (Shawinigan technology), which leads to yield in water-cooled jacketed cylindrical retorts [51].

The apparatus consists of a “burner” which serves to introduce the gases into the decomposition chamber, a refractory to form a retaining wall for the reacting gases and auxiliary equipment to remove the acetylene black from the hydrogen. The decomposition reaction starts by burning a mixture of acetylene and air. Thereafter, the air is closed off and decomposition continues, as acetylene decomposition is an exothermic reaction (ΔH_{293} = – 230 kJ/mol). The formation of aggregates requires more primary particles to join the formation of the aggregate and that leads to a much higher aggregate structure. Other hydrocarbons are usually added to acetylene to prevent the reactor temperature from rising due to the exothermic reaction. The temperature is maintained at the desired level by water cooling. The production of acetylene black is shown in Figure 2.10.

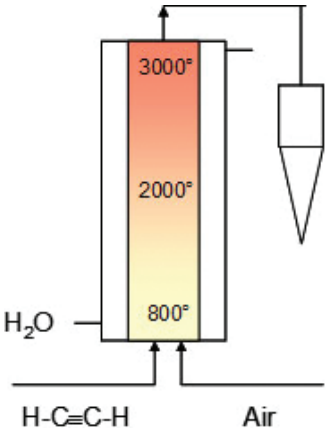

Figure 2.10
Acetylene black process

The carbon black is separated from the hydrogen, degritted and packed in paper bags, uncompressed or compressed. The tail gas, hydrogen, is flared or used as a fuel. Continuous processes were developed with a production rate of 500 kg/h. Although the medium primary particle size of acetylene black is in the same range as that of the furnace blacks, the structure diverges from the spherical form. Acetylene black consists of carbon particles with a high content of sp^2 hybridization (graphitic layers) that provide quite high electrical conductivity. To achieve comparable electrical conductivity in a compound, only small levels of these types are needed, compared with standard furnace blacks. Acetylene carbon blacks are normally fluffy and have a low bulk density of 19 kg/m^3. They are difficult to compress and resist the process of pelletization. They can be compressed to a bulk density of up to 200 kg/m^3. Acetylene carbon black is very pure and has a carbon content of 99.7%. It has an average particle diameter of 40 nm and a surface area of 65 m^2/g and a high structure of 250 mL/100 g. It has unconventional laminar particles that are larger than those of furnace black N 330. Acetylene carbon blacks are much more expensive than furnace carbon blacks. The high proportion of sp^2 hybridization makes acetylene carbon black suitable for highly electrically conducting applications and also thermal applications.

2.1.3 Pellet Size and Hardness

The hardness of individual pellets is related to the size of the pellets and the average pellet hardness. The pellet hardness stated in product certificates only provides information about the average value. In most applications, the carbon black cannot be used in its original fluffy form as produced in the furnace process. The filler particles need to be compacted in the form of pellets to survive transportation, storage in silos and handling in the mixing chamber, without generating dust. Special tests have been developed for measuring the ability of the pellets to disintegrate and pack during bulk

handling and for measuring the degree of dispersion in a polymer [52, 53] The ASTM method involves crushing a total of 20 pellets from which the results obtained at high and the low force are eliminated, because they are not as relevant. For pellets of the same matrix, there is a direct relationship between size and hardness. Therefore, pellet size must be specified when describing pellet hardness. Individual pellet hardness is measured according to a standard procedure [54]. Wet-pelletized and dry-pelletized carbon black are shown in Figure 2.11.

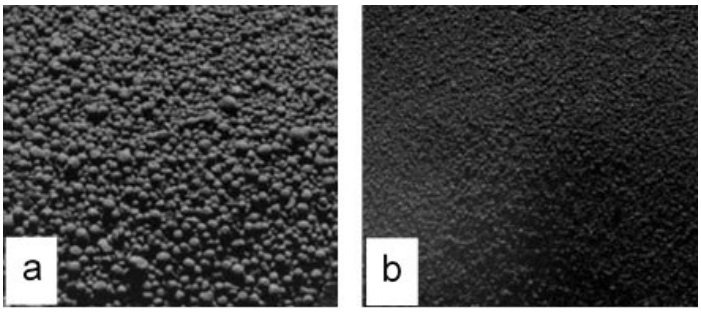

Figure 2.11 Pelletized carbon black: a) wet-pelletized and b) dry-pelletized

The pellet hardness test [55] involves applying an increasing force to a single pellet unit until it breaks. The breaking force varies with pellet size, so the carbon black industry uses the –12/+14 mesh fraction. Compounds that use low-viscosity polymers usually require soft carbon black pellets. The pellet hardness is related to pellet fragility and therefore abrasion resistance. Pellets that are too hard can cause problems with carbon black dispersion, especially in soft compounds. Softer pellets make for better dispersion, but their inherent propensity towards fineness may create handling issues. Wet-pelletized carbon blacks are usually characterized by greater pellet hardness than dry-pelletized carbon blacks. Pellet strength and hardness should not exceed a certain level, which is determined by the ease of fragmentation and dispersion during mechanical mixing. The recommended hardness for carbon blacks is in the range of 5–20 g for pellets of 1 mm or less than 15–30 g for larger pellet sizes. Pellet hardness becomes critical if the viscosity of the compound is low or if the plasticizer oil content is high. Such compounds may require a pellet hardness of less than 30 g. Pelletized carbon blacks offer advantages over powder carbon black from ecological and application-related aspects, such as dust loading, good flow behavior, ease of filling and meterability.

The pellet size distribution is a parameter that affects the flow characteristics of pelletized carbon black. A uniform pellet size means optimum flow behavior, which is recommended for automatic feeding of carbon black into an internal mixer. The fines content of carbon black pellets is also determined. Fines content in carbon black is

undesirable for several reasons, not least because of problems associated with dusty material. Excessive fines can lead to problems with dustiness and flowability.

The production process, especially in the vertical furnace, also produces carbonaceous impurities, known as grit, which are larger than the carbon black aggregates and present certain challenges when carbon black is used as a filler in rubber compounds. The presence of grit adversely affects the polymer matrix into which the carbon black is dispersed and significantly lowers the tensile strength and other mechanical properties. The grit content must be removed or significantly reduced to become an integral part of the matrix. The amount of grit present in a sample of carbon black is measured by washing a given quantity of the carbon black on a specified screen size [56]. The insoluble residue, expressed in mg/kg (or ppm) of the original sample, provides indication of the quality of the carbon black. The smaller the grit, the greater is its ability to improve the properties of the rubber compounds. However, the presence of grit can dramatically shorten the life of the screens and the extrusion dies used in tire manufacturing. Grit size reduction can be achieved by grinding in long-gap mills or air-classifying mills.

2.1.4 Purity of Carbon Black

The purity of carbon blacks is generally assessed on the basis of toluene discoloration [57], ash content [58], grit residue [59] and sulfur content [60]. Toluene discoloration gives a rough indication of extractables present on the surface of carbon blacks. In carbon black with a lot of tar, the toluene extract is dark yellow in color. The main sources of grit are coke that forms in the reactor, pieces of the refractory that have eroded from the reactor and metals from the process equipment. The aim is to produce carbon black without the various impurities.

2.1.5 Classification of Carbon Black

As a large number of carbon blacks are used, the development of a more rational nomenclature for new types of carbon black was inevitable. The classification system introduced for carbon black is based on a nomenclature consisting of four characters. However, the classification is far from perfect, particularly because the last two digits are arbitrarily assigned. The ASTM classification and the type code used in the past are shown in Table 2.4. The classification is used to distinguish between the:

- influence on vulcanization speed
- primary particle size, and
- structure of the carbon blacks

The first character in the classification system is a letter that indicates the effect of carbon black on the curing rate of a compound containing the carbon black. Thus, N stands for carbon blacks that do not change the curing rate and S is used for blacks that slow down the curing rate (e. g. channel black). The second character refers to the nitrogen specific surface area, which is arbitrarily divided into nine classes, each of which is assigned a digit that describes the range of the specific surface area. The third and fourth characters are digits that describe the "structure" of the filler aggregate. A normal structure corresponds to 100 mL oil/100 g carbon black, as is the case for N330. A carbon black with a higher structure is indicated by a higher number (e. g. N339) and a carbon black with a lower structure by a smaller number (e. g. N326).

Table 2.5 Classification of Carbon Blacks

ASTM Classification	Generic Name	Type	Nitrogen Spec. Surface Area (m^2/g)	Average Particle Size (nm)
N 110	SAF	Super-abrasion furnace	130	11–19
N 220	ISAF	Intermediate-abrasion furnace	115	20–25
N 330	HAF	High-abrasion furnace	79	26–30
N 550	FEF	Fast-extrusion furnace	41	40–48
N 660	GPF	General-purpose furnace	35	49–60
N 762	SRF	Semi-reinforcing furnace	28	61–100
N 990	MT	Medium thermal	9	200–500

The table also shows a use of carbon black, taken from an older classification, which is still used today in many companies, like high abrasion, fast extrusion or general purpose furnace black. Although the classification could be improved to include the processability of carbon blacks, it has been used in rubber technology for half a century and there is sign yet of any improvements being made.

2.1.6 Global Production of Carbon Black

Carbon black is the most commonly employed reinforcing filler in rubber technology. Most than 92% of global production of carbon black is used in the rubber industry, especially in tire production. The remaining 8% is used for non-rubber applications, for pigments, plastics, and coatings. About 13.9 million metric tons of carbon black were produced worldwide in 2016, placing it among the top 50 industries. A typical tire contains 30–35% carbon black, and there are several different grades in the tire, depending on the reinforcement requirements. An almost equally large amount, 2–3 million metric tons, is used for the manufacture technical products, owing to its ability to reinforce other rubber components and reduce production costs. The leading producers of carbon black in the world are:

- Cabot Corporation 43.5%
- Birla Carbon 15.7%
- Orion Engineering 15%
- Black Cat 8.6%
- Tokai Carbon 6.8%
- Others 6.4%

The use of carbon black in various end-use rubber industries is important for the progress of production in tires and technical rubber goods. The global market has been expanded through the use of carbon black for tire construction. Despite the climate-mitigation measures being discussed today, demand for carbon black remains strong, as an outstanding filler that keeps the properties of tires and technical rubber goods at a high level. The growth in demand for carbon black in the automotive industry is driving the overall carbon black market. It will be interesting to see how things develop over the next 20–30 years, once the discussions on climate protection have taken hold, especially when electric cars are introduced, which can reach high speeds more quickly.

2.2 Amorphous Silica

Precipitated silica is a polar filler that is synthesized in an aqueous slurry from water glass and a strong mineral acid. About 70% of synthetic precipitated silica is processed in the rubber industry. It is an important nanofiller that is becoming increasingly important in passenger tire production and technical rubber goods. It has evolved from a simple filler used for colored rubber products to a functionalized filler with organosilane that is able to improve the reinforcement of unsaturated rubbers, especially to

reduce rolling resistance and increase the wet grip of car tire treads. The use of amorphous silica has increased exponentially over the last three decades since it was first used in tire-tread compounding [61–66]. By manufacturing it in a slurry solution, it is possible to obtain the desired result with a defined morphology and different particle size and high structure in a rapid process. As the process is fast enough to prevent the formation of silica crystallites, the silica produced has an amorphous structure. There are two methods for the rapid production of amorphous silica:

- precipitated silica made in a solution reaction
- fumed silica produced by pyrohydrogenation

Both yield amorphous silica, but the essential difference is the amount of polar silanol groups that are present on the silica surface. The first method is a solution process while the second is much faster and takes place in the gas phase. As the starting chemicals are different for precipitated silica and fumed silica, therefore the manufacturing processes are also different. The difference between the two methods is the size of the primary particles and the number of silanol groups on the aggregates.

The use of organo-silanes converts the “water friendly” or hydrophilic precipitated silica into “water-repelling” or hydrophobic silica that can be used for much better interaction with the rubber chains of unsaturated non-polar rubber [61, 67]. A variant is the *in situ* manufacturing of precipitated silica in the rubber network from a soluble form of silica in an organic solvent [68, 69]. However, this type of well dispersed silica nanoparticle is only of academic interest. Of course, the use of the same particle size description for precipitated silicas and carbon blacks does not imply the same level of reinforcement. It is known that silicas and carbon black of the same particle size normally do not provide the same level of reinforcement, because the interaction with the rubber is based on different principles. The difference disappears when coupling agents, such as organo-silanes, are used with silica. Organo-silanes improve rubber-filler interaction and decrease polar filler-filler interaction. The silica and the carbon black of similar size then provide equivalent reinforcement, as measured by modulus, tensile strength and tread wear.

2.2.1 Manufacture of Precipitated Silica

Precipitated silica is produced by precipitating an aqueous solution of sodium silicate (water glass) with a mineral acid, usually sulfuric acid. The sodium silicate is produced by alkaline fusion of high-purity quartz sand and sodium carbonate at high temperatures, a process which is energy intensive and expensive. As a salt, water glass is soluble in water [61, 62, 65, 66]. The chemical reaction for the synthesis of amorphous silica is:

$$SiO_2 + Na_2CO_3 = Na_2SiO_3 + CO_2$$
$$Na_2SiO_3 + H_2SO_4 = SiO_2 + Na_2SO_4$$

Once a defined pH value has been set, the components are fed continuously into the reactor. This process takes place simultaneously over a certain period of time in order to ensure consistency of product morphology. Another option is to first feed in a certain quantity of water glass and an initial dose of sulfuric acid and then to dose both simultaneously under defined reaction conditions. Precipitation, which occurs on overly rapid addition of concentrated acids, produces a small amount of silica gel. This gel content has no adverse effect on reinforcement, but can be a significant source of non-dispersed silica for the customer. The resulting filler has a higher proportion of silanol groups on the filler surface which make the surface of the aggregates acidic.

The primary particles consist of amorphous SiO_2 and a small number of acidic silanol groups (Si-OH) situated on the surface of the particles. Subsequently, the primary particles react with each other by eliminating water, forming siloxane bonds (Si-O-Si) on the surface of the aggregate. Formation of the agglomerates depends on the reaction time, the pH and the electrolyte. A state of equilibrium is reached between the aggregates and the agglomerates which depends on the process conditions and can be influenced by the process operator. Depending on the intended application of the precipitated silica, the process conditions such as feed rates, stirring, precipitation parameters, temperature, pH, alkali content etc. can be adjusted to provide a wide range of products of different properties. Between pH 3 and 6–7, a silica gel is formed, but it is not easily dispersed in elastomers. The usual pH range for commercial precipitated silica is 8.0–8.5, so that precipitated silica can be dispersed in rubber compounds [65, 67].

The resulting suspension is transferred to a homogenizer to reach the end point of the chemical reaction to produce amorphous silica. Precipitation parameters involved in setting the particle size include temperature, reaction rate, reactant concentrations, and the presence of additives in the silica. The precipitation temperature correlates with particle size; low temperatures produce small silica particles. Slow rates of neutralization reduce gel formation [71]. The aqueous suspension of silica particles is filtered and washed to remove traces of the mineral acid and sulfates. Since the solids content of the filter cake is 15–25% water, this must be removed from the filter cake.

Several types of dryers are utilized in the production of silica: rotary drum dryers, spray dryers and spin flash dryers. For the production of 100 kg of precipitated silica, 400 kg of water must be evaporated. The dried product still contains 10–14% water and needs to be finely milled. In line with the drying step employed, the precipitated silica may be milled and then granulated or granulated directly into a low-dust product [72, 73]. Special product properties can be achieved by spray-drying the filter cakes after redispersion in water or acid [74]. Both the size of the particles and the surface activity (see below) can be controlled within relatively narrow limits via the choice of processing parameters [75].

After the homogenizer, the product is sent for washing and filtering. Acid precipitation produces a slurry of silica and residual salts (sodium sulfate). The salts are removed by washing in a counter-current decanter or by means of a filter press. Wash-