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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 applications. 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 crosslinked 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.

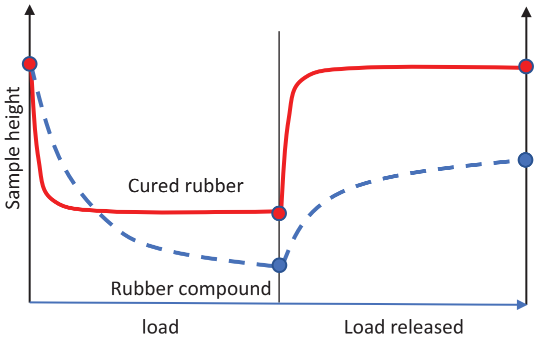

Figure 1.1
Response to a filler force acting on the mixed compound and the vulcanizate

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