

Why is vulcanised rubber such an important soling material for the footwear industry? In this, the first part of a two-part feature article, *World Footwear* looks at its background and explains how it works.

Vulcanised rubber (part 1)

For over 2,000 years, the sap of the Hevea Braziliensis tree has been dried to extract a material called polyisoprene, which we know better as natural rubber (NR). In this basic form it possesses rubber's property of substantially returning to its original shape after being stretched, but also becomes very sticky in hot conditions and very stiff in cold ones.

It was not until the 19th century that significant progress was made in modifying the performance of natural rubber. In London in 1819, Thomas Hancock invented the first internal mixing machine to mechanically work the rubber, making it softer and easier to process. He then moved on to using the American-designed two-roll mills, which would be used by the industry for over a hundred years, before the re-appearance of the internal mixer in the early 1900s.

The next key step was the blending of natural rubber with sulphur and then heating the mixture. This process was developed by both Goodyear in the USA and Hancock in England around 1841-1843 and it was his friend William Brockedon who first used the term vulcanisation for this process after Vulcan the god of fire. The words vulcanise, cure, and cross-link all refer to the process that alters the structure of isoprene by introducing cross-links. The vast majority of rubber products today owe their existence to this process. In 1904 it was found that blending carbon black into the rubber significantly increased a number of its mechanical properties.

In 1910, the Russians developed the first synthetic rubber polybutadiene (BR) and, in the 1930s, the Germans began commercial production of a synthetic rubber called Buna-S (styrene butadiene copolymer). These rubbers were improved in the United States during the 1940s, leading to the SBR which is the major material used in the rubber industry today. The main grades used in the preparation of vulcanised rubber for footwear applications are NR, SBR and two other synthetics, nitrile butadiene rubber (NBR) and isobutylene isoprene copolymer (IIR). The final compound to be vulcanised is normally based on a mixture of 100 parts of the basic rubber plus polymers, fillers and other additives combined at various levels to assist the vulcanisation process and measured as parts per hundred (phr) of the rubber.

VULCANISATION

Unvulcanised rubber consists primarily of long polymer chains entangled like a mass of elastic fibres which, when stretched, disentangle, slip over each other and tend to straighten out. As previously mentioned, it also has poor resistance to heat and cold. The traditional method of vulcanisation using heat and



sulphur forms cross-links between the polymer chains which greatly decrease the amount of slippage. As well as making the rubber far more dimensionally stable and heat resistant, vulcanisation also improves and stabilises its physical properties.

CROSS-LINKING

Sulphur is still the main cross-linking agent used and works by linking one polymer chain to another by opening the double bonds. To achieve the required level of vulcanisation for NR and SBR only a small percentage of the double bonds needs to be linked and this can be achieved with 2-3 phr of sulphur using a conventional cure system. Unfortunately, this leaves a large percentage of double bonds unused and therefore vulnerable to attack by oxygen, ozone and heat. If, on the other hand, a higher level of sulphur (greater than 30 phr) is added, the cross-linking is increased to such an extent that the final compound becomes very hard at around 70D—even without fillers—and also very inelastic, with an elongation at break of about 5%.

Whilst sulphur and heat together will vulcanise the rubber

matrix it is a slow and not very efficient system, so activators such as zinc oxide and stearic acid plus accelerators are needed to speed up and control the process. When the balance of these additives is correct then an efficient vulcanisation (EV) system is said to have been achieved.

Too much sulphur leads to weaker S-S internal bonds which are less thermally stable and also result in poorer compression set. On the other hand, they increase flexibility and fatigue life while also reducing stress in a component. It is therefore clear that the selection of the cure profile depends very much on the required performance of the cured rubber.

Peroxides are an alternative to sulphur, which do not need a double bond and act through the formation of free radicals on the polymer chain by removing hydrogen atoms. Carbon to carbon bonds are formed, which are much stronger than carbon to sulphur, more thermally stable and have better compression set. Unfortunately, they also tend to have poorer tensile and fatigue properties. NBR and SBR, the two main rubbers used in footwear, can both be vulcanised using peroxides, so, together with all the types of sulphur cure, there is a very wide range of curing alternatives available to compounders.

ADDITIVES

As well as the additives needed to achieve the correct cure, other additives are needed to ensure that the expected properties and life expectancy are obtained from the final vulcanised rubber. The early role of carbon black has already been mentioned, but it is necessary to point out that it is not just used as a pigment to produce a black rubber, but mainly because it reinforces the rubber and greatly improves its physical properties. Other commonly used fillers are silica and calcium carbonate.

There are three basic types of plasticiser used in rubber formulations, all based on petroleum oils: aromatic, naphthenic and paraffinic. The choice of which to adopt depends very much on the rubber matrix being used, its ability to absorb oil and which final properties are required.

As many formulations require the addition of reinforcing fillers to achieve the desired properties, a large proportion of finished products end up being black due to the use of carbon black. However, there is now more and more demand for brightly coloured rubber products—especially footwear—and an increasing range of suitable pigments is now available.

There are also times, such as when moulding large complex parts, when it is necessary to slow down the vulcanisation

process at the start of the reaction and, to do this, retarders are added. Antidegradants are also needed in order to protect the finished component from ageing due to attack from oxygen, ozone, UV and heat, and a wide range of compounds are available to meet this function, most of which are free radical scavengers, the main cause of the degradation.

TYPICAL ADDITIVES

Function	Additive
Accelerators	Dithiocarbamates, Guanidines, Sulfenamides, Thiazoles, Thiurams
Activators	Zinc Oxide and Stearic Acid
Antidegradants	Antioxidants, antiozonants (p-phenylene diamines), UV stabilisers
Fillers	Carbon Black, Silica,
Pigments	Carbon black, TiO ₂ , coloured pigments
Plasticisers	Aromatic, naphthenic and paraffinic oils
Retarders	Benzoic acid, phthalic anhydride, salicylic acid
Vulcanisates	Sulphur and peroxides

MIXING

Once a formulation has been devised, the chips, lumps or granules of raw rubber, bags of powder and drums of liquids must be turned into a homogeneous useable material. These must be precisely weighed and carefully mixed to achieve the finely blended compound required without setting off the vulcanisation process or damaging any of the components. There are two main methods of doing this.

Milling involves two horizontal hollow metal cylinders rotating towards each other where the gap or 'nip' between them can be varied from 2mm to 20mm. These rotate at different speeds with the back roll running about 25% faster than the front one. This difference in speed, known as the friction ratio, allows a shearing action at the nip to disperse and heat the ingredients, and force the compound to stay on one cylinder only—preferably the front one.

To start the process the raw gum rubber is loaded into the gap between the two mill rolls and run until it forms a continuous sheet. Then the powders, liquids and oils are added in a specific order, usually derived from experience and trial and error. The heat produced by the process needs to be removed and this is achieved by passing cooling water through the rolls. As the rubber mix both falls off the mill and tries to move past the end of the cylinders, it is necessary to fit guides to keep the material in place and return fallen pieces to the nip. Once the ingredients are fully blended the continuous sheet can be cut and removed in one piece.

Mixing involves a machine consisting of two rotor blades turning in a chamber with a top hopper to load materials, a ram to force the material into the mixing chamber and a discharge door at the bottom. The best known machine is probably the Banbury, where the heat is removed by channels drilled into the walls of the mixing chamber. Good mixing is obtained by correctly setting the rotor-rotor and rotor-wall clearances. The use of internal mixers has tended to displace milling since it is cleaner, faster and less reliant on operator skill. 

Part 2 will look at how the compound is moulded into a finished shoe sole.

The FiveFinger sole from Vibram is a good example of modern design and colour

