

Vibram's FiveFinger sole is a good example of modern rubber moulding.

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Footwear Fundamentals

Vulcanised rubber

Natural rubber (NR) has been known for hundreds of years. In its natural form, it was not suitable for use in footwear as it was too elastic, became sticky in hot conditions and hard and brittle in the cold. It was not until the 19th century that it became possible to modify it sufficiently for footwear use. The first step came in 1819 with the invention of an internal mixing machine that made it softer and easier to process.

The most significant advance, however, came in the early 1840s with the addition of sulphur and subsequent heating of the mixture, a process called vulcanisation, which made it more stable. In 1904 it was found that introducing carbon black significantly increased its mechanical properties. In 1910, the first synthetic rubber (polybutadiene or BR), was developed to be followed by Buna-S (styrene butadiene copolymer) in the 1930s.

SBR

These synthetic rubbers were further improved during the 1940s to produce styrene-butadiene rubber (SBR) which is the major material used in the rubber industry today. The main footwear grades are NR and SBR, plus 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 to assist vulcanisation and measured as parts per hundred (phr) of the rubber content.

VULCANISATION

Unvulcanised rubber consists primarily of long polymer chains entangled like a mass of elastic fibres which, when stretched, disentangle and slip over each other as they straighten. Traditional vulcanisation using heat and sulphur forms cross-

links between the polymer chains which greatly decreases the amount of slippage. As well as making the rubber more dimensionally stable and heat resistant, vulcanisation also improves its physical properties.

CROSS-LINKING

The sulphur links one polymer chain to another by opening the double bonds. With NR and SBR only a small percentage of these needs to be linked and can be achieved with 2-3phr of sulphur using a conventional cure system. Unfortunately, this leaves a large percentage of double bonds unused and vulnerable to attack by oxygen, ozone and heat. If more than 30phr is added, cross-linking is increased to such an extent that the final compound becomes very hard at around 70D even without fillers, very inelastic and with an elongation at break of about 5%.

TYPICAL ADDITIVES

FUNCTION	ADDITIVE
Accelerators	Dithiocarbamate, guanidines, sulfenamides, thiazoles, thiurams
Activators	Zinc oxide, stearic acid
Antidegradants	Antioxidants, antiozonants, UV stabilisers
Fillers	Carbon black, silica, calcium carbonate
Pigments	Carbon black, TiO ₂ , coloured pigments
Plasticisers	Aromatic, naphthenic and paraffinic oils
Retarders	Benzoic acid, phthalic anhydride, salicylic acid
Vulcanisates	Sulphur and peroxides

Vulcanisation using just sulphur and heat is slow and not very efficient, so activators such as zinc oxide and stearic acid plus accelerators are needed to speed up and control the process. A correct balance results in efficient vulcanisation (EV). Too much sulphur leads to weaker internal bonds which are less thermally stable and also result in poorer compression set. On the other hand, they increase flexibility and fatigue life, so it is clear that selecting the cure profile depends very much on the required performance of the cured rubber.

Peroxides are an alternative which do not need a double bond and act by forming 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 can both be vulcanised using peroxides so, together with all the types of sulphur cure, there is a wide range of possibilities for compounders.

ADDITIVES

As well as these additives, others are needed to ensure that the expected properties and life expectancy are obtained from the final vulcanised rubber. Carbon black is still used to reinforce and improve physical properties, while silica and calcium carbonate are commonly employed as fillers. Three types of oil-based plasticiser are also used, aromatic, naphthenic and paraffinic. Final choice depends on the rubber mix being used, its ability to absorb oil and the final

properties required.

Complex mouldings may also call for retarders to slow the vulcanisation process at the start of the reaction. Anti-degradants are also needed to protect the final component from ageing through attack from oxygen, ozone, UV and heat. A wide range of compounds is available to meet this function, most of which are free radical scavengers, the main cause of the degradation.

BLENDING

Once a formulation has been finalised, the various ingredients must be precisely weighed and carefully mixed to achieve a final homogeneous, blended compound without setting off the vulcanisation process or damaging any of the components. There are two main methods of doing this.

Milling blends the ingredients between two horizontal metal cylinders rotating towards each, with the rear one approximately 25% faster than the front, and where the gap or 'nip' between them can be varied from 2mm to 20mm. The difference in speed creates a shearing action at the nip to

disperse and heat the ingredients and force the compound to stay on one cylinder only.

Raw gum rubber is loaded into the nip and run to form a continuous sheet to which the powders, liquids and oils are added in a specific order based on experience. Heat is removed by passing cold water through the hollow cylinders and end guides keep the mix centred on them. Once the ingredients are fully blended the continuous sheet can be cut and removed in one piece.

Mixing uses two blades rotating in a chamber with a top hopper to load materials, a ram to force them into the mixing chamber and a discharge door at the bottom. The best known machine is the Banbury, where heat is removed by channels drilled into the walls of the mixing chamber. Good mixing is obtained by correct setting of the rotor-rotor and rotor-wall clearances. This type of mixing has largely replaced milling as it is cleaner, faster and less reliant on operator skill.

VULCANISED SOLING

Vulcanised rubber unit soles have traditionally been made using compression moulding in single or multiple hydraulic presses heated to a temperature of 160-180°C. Partially-vulcanised milled rubber sheet is cut into blanks to fit the mould cavity plus an extra piece for the heel. These are pre-heated to around 110°C to reduce cycle time and manually loaded into the moulds. The press is closed and the components compressed for between four to ten minutes until the rubber is fully vulcanised. Blanks usually weigh 2-8% more than the required final weight as the excess material ensures the mould is fully filled and all the air forced out when the press closes.



Rubber overshoe marked Goodyear patent 1858.

CREDIT: M WOSHNER

Desma rubber extrusion head.

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SPECIAL DEMANDS

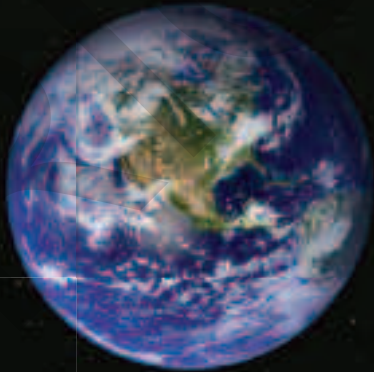
Obtaining a good bond between the vulcanised rubber and PU was not easy however. Desma solved the problem by using an injector head that tracks over the piston in the open mould and extrudes pre-vulcanised rubber along its length as 'spaghetti'. This is then vulcanised by closing the mould and applying heat. When the mould opens prior to injecting the PU, a robot head sprays the surface of the vulcanised outsole with an adhesive that bonds it securely to the PU. The resulting sole combines the durability of rubber with the light weight and shock absorbency of polyurethane. 

DIRECT MOULDING

This uses four-part moulds consisting of a sole mould or piston, two side moulds and a metal foot/last. Because of the high pressure used, the moulds have to be securely fixed to the machine and are difficult to change quickly. In operation a roughed and cemented upper is force-lasted on to the foot, the pre-heated sole blank placed on the piston, the foot positioned over it, the side rings closed on to the lasted upper and the piston moved upwards to a preset level. The rubber melts, flows to fill the mould evenly and vulcanises itself to the upper. At the end of the cycle the mould opens automatically and the foot rises so that the completed shoe can be de-lasted and the cycle repeated.

INJECTION MOULDING

Main Group in Italy introduced its Incom Process in 1992. This featured a nozzle that could be inserted through the back of the mould so that the rubber could be injected as a ribbon rather than inserted as a blank. The new system made it possible to produce direct moulded footwear with either a solid vulcanised rubber outsole or a combination of a thin solid outsole and a thicker, lower density blown rubber midsole. At the same time Desma in Germany produced a system that replaced the blown rubber with microcellular PU which proved so successful that it is still in extensive use today.



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