Chapter 2

Historical review of soling materials

2.1 Historical Review

Leather was used as the traditional soling material before the invention of synthetic rubber and plastics. Soles cut directly from crepe natural rubber were also used but not successful. Later in early part of the nineteenth century vulcanised natural and synthetic rubber were employed. SBR- styrene-butadiene rubber, synthetic rubber of high abrasive resistance has been found to be better than the vulcanisate of natural rubber for this purpose. During the last fifty years many rubber and plastics have been tried out of which the following are popular for their advantageous properties.

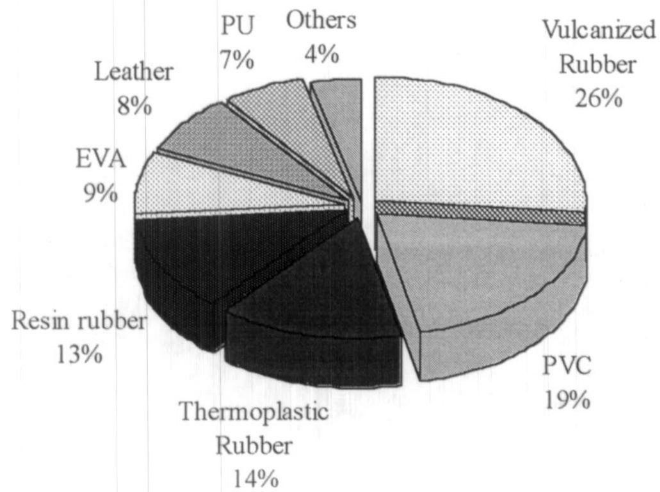
2.2 Shoe Soling Materials, their main features and applications

Material	Main features	Applications
Leather:	Traditional soling materials cut from tanned animal hides provide strong aesthetic appeal and gives high quality image. Major leather exporting countries are Argentina, Mexico and Italy	High class footwear
Natural Crepe Rubber:	A material based on natural latex tapped from rubber trees, low level of resistance to solvents and oils, good durability and flexibility. Major suppliers are Malaysia, Indonesia and Thailand	Casual footwear and Children's sandals
Vulcanised synthetic Rubbers:	Versatile Materials, The soles are compression moulded. Base polymers are SBR, polyisoprene rubber, polybutadiene rubber, Polychloroprene rubber, nitrile rubber, and natural rubber	Every day footwear Sports shoes Industrial boots Sandals Slippers

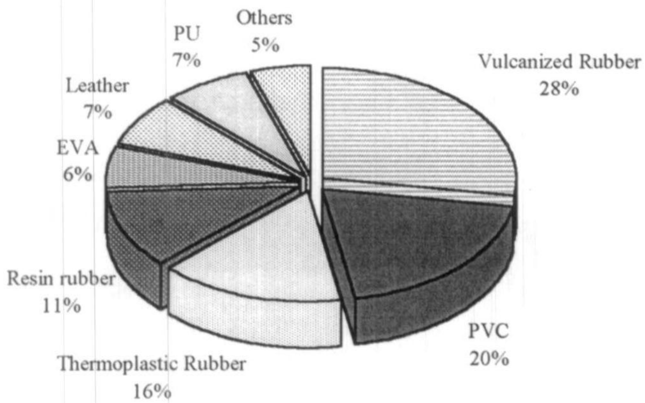
Resin- Rubber	Vulcanised rubber reinforced with high styrene resins. Base polymer is usually SBR, Styrene content is 50 –85 %. Hard flexible and reasonably durable	Everyday footwear Women's court shoes and Casuals
Poly Vinyl Chloride (PVC)	Widely used for injection moulding soles, good durability, smooth in wear and crack resistance tends to be low in cold climates PVC can be blended with nitrile rubber, Poly Urethane (PU) and Ethyl Vinyl Acetate (EVA) for special applications	Everyday footwear and Industrials footwear
Thermoplastic Rubber (TR)	Soles are made from injection moulding Although a plastic looks and feels rubbery. Their cellular versions can be produced with blowing agent. They are durable and having good slip resistance, on the other hand good flex resistance at low temperature. So suitable for use in cold climates. Base polymer is SBS (styrene butadiene styrene) block copolymer, combining rubbery butadiene with thermoplastic styrene chemical structure.	Everyday footwear
Poly Urethane (PU)	Reaction moulded cellular polyurethane offers a broad range of densities and hardness. Light, flexible, and durable	Sports, Safety, Casuals and Everyday footwear
Ethyl Vinyl Acetate (EVA)	Available as microcellular sheet form and injection moulded units. Very light soling materials. Cross-linked synthetic copolymer of ethylene and vinyl acetate. Flexible and good shock absorption. Durability and slip resistance are limited for outsole	Mid-soles Inserts in Sport shoes and for Sandals

2.3 World's Usage of soling materials

i) In 1999



ii) Projected usage for 2005



(From "World Soling Market"- SATRA Footwear centre, England –1999)

2.4 Density of the soling material

Density, the mass per unit volume is the chief characteristic of soling materials. The range of density values generally varies from 0.2 to 1.4, as given in the following Figure 2.3.

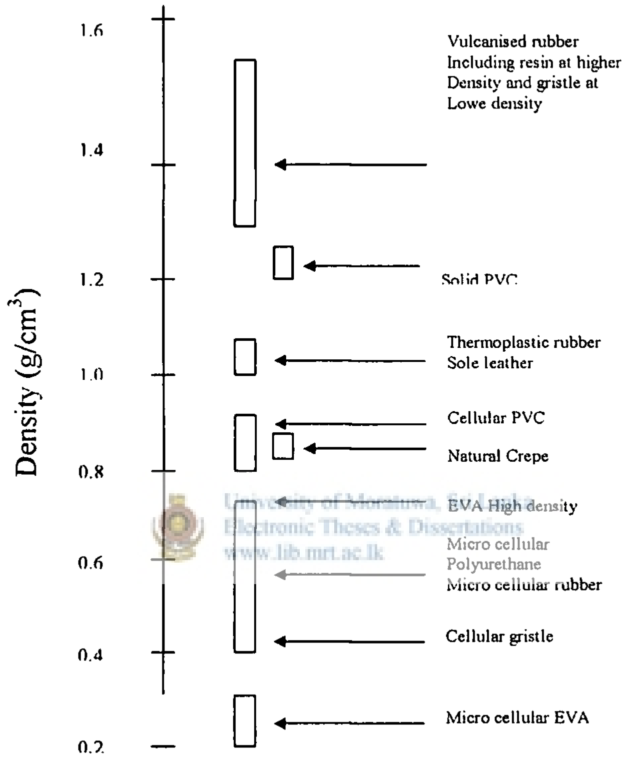


Figure 2.3 Density ranges of soling materials (From "Current Guideline for Commonly used Soling" - SATRA footwear centre, England - 1998)

2.5 Physical properties of standard resin soling

The standard resin soling is characterised by the following main physical properties: Tensile properties, Hardness, Density, Abrasion Resistance and Flex Resistance.

Tensile properties

The maximum load to break per original area of the cross section of the mid portion of the dumb bell is called as tensile strength

Hardness

A hardness measurement is a simple way of obtaining the mechanical properties of resin soles. The purpose of conducting hardness test is to determine the elastic modulus of a rubber under conditions of small strain by determining its resistance to rigid indenter pressed with a force on the surface of the product.

Abrasion Resistance

Abrasion Resistance is a performance factor of paramount important for resin soles. The sample abraded by processing in surface against an abrasive surface, with a predetermined force. The volume loss in rubber is calculated as per standard formula, which will be described under testing methods.

Flex resistance

Flex resistance of resin sole is a performance characteristic in service and very important and define as resistance to deformation in bending.

Shoes and Allied Trades Research Association (SATRA) in United Kingdom is the one of the recognized technology centres for the research and development of shoe materials. This association provides valuable technical assistance and guidelines for most of the shoe manufacturing industries in the developing countries, today. SATRA guideline recommendations for physical properties of resin- rubber sole sheets are given in the Table 2.1.

Table 2.1 SATRA Guideline Recommendations for Resin rubber sole sheets (From "Current Guideline for Commonly used Soling" - SATRA footwear centre, England - 1998)

Test Method	**Property**	**SATRA Recommendation**
SATRA TM 206 1999	Hardness (IRHD) @ 23 ° C	≥ 88
SATRA TM 134 1998	Density (g/cm^3)	≤ 1.50
SATRA TM 137 1995	Tensile Strength (Mpa) Dumb-bell Type: 2	≥ 6.5
SATRA TM 137 1995	Extension at Break (%) Dumb-bell Type: 2	≥ 200
SATRA TM 60 1992	Ross Flex @ – 5 °C mean cut growth rate (mm/kc)	≤ 0.05
SATRA TM 174 1994	Abrasion Resistance Volume Loss (mm^3)	≤ 400

Resin shoe soles sheet dimensions

Length	Standard	1000 mm
Width	Standard	1000 mm
Thickness	Standard	2.5, 2.7, 3.0, 3.5, 4.0, 4.5 mm
	Non standard	2.2, 5.0, 6.0 mm

2.6 Survey on resin- rubber sole compounds used in Sri Lankan Industries

Before 1990 Elastomeric Pvt Ltd manufactured resin- rubber sheets for domestic use. In 1998 Arpitalian Compact Soles (Pvt.) Ltd, a joint venture of Richard Pieris Group of Companies, one of the most experienced and reputed organization involved in the rubber production industry and Davos s.p.a, a world reputed shoe sole manufacturer from Italy started manufacturing resin- rubber sole and heel sheet as a soling material for women's, men's and children's everyday footwear. Davos has provided the technical expertise to set up Arpitalian's manufacturing facility and it is one of the most modern resin- rubber sheets manufacturing and painting plants in South Asia.

Original compound formulation (See Table 2.1) was introduced to Arpitalian by Davos s.p.a in 1998 and commercial production was started using that formulation. Original formulation contained about 15 ingredients. Styrene Butadiene Rubber (SBR 1502) was used as rubber and high styrene resin as resinous filler and kaolin, buffing dust, silica calcium carbonate, zewa harz pulver, and wood flour as fillers. Aktiplast pp and coumarone- indene resin (rhenosin C 90) were used as processing, activating and dispersing agents. Other chemicals, which contained in the original formulation, were carbon black as reinforcing filler, zinc oxide as an inorganic activator, and N-Cyclohexyl -2-benzothiazyl-sulfenamide (CBS) and Diphenyl guanidine (DPG) as accelerators. Sulphur was the vulcanising agent used in original compound formulation.

Table 2.7: Standard formulation, which was introduced by Davos s.p.a Italy to start commercial production at Arpitalian a leading Sri Lankan resin sole manufacturing company, in 1998

Ingredient	**Amount (phr)**	
SBR 1502	55	100
High Styrene (HSR 65%)	45	
Calcium Carbonate		40
Kaolin (400 µm)		30
Buffing Dust (30- mesh)		30
Silica (VN3)		10
Carbon Black (N330)		10
Coumarone- indene resin (Rhenosin C 90)		6
Wood flour		10
Zewa Harz Pulver		7
Aktiplast PP		2
Zinc Oxide (99.7)		4
CBS		2
DPG		.5
Sulphur (Rubber Grade)		3

In this compound, only calcium carbonate and kaolin were used as local raw materials. All other raw materials were imported. As a result of that the raw material cost was 70 % of total cost of manufacturing of resin rubber sheet.

Rubbers used

Styrene- Butadiene Rubber (SBR)

SBR is copolymer of styrene and butadiene. It is the most widely used type of synthetic rubber. SBR provides superior uniformity and cleanliness. Proper compounding has expectation of high resistance to abrasion and heat, compared to natural rubber. Its extrusion properties are superior to those of natural rubber, and stocks have less tendency to scorch in processing. SBR1502 was used in original formulation (See Table2.1) for resin-rubber soles. SBR are used in tire treads, hoses, rubberised cloths, conveyor belts, and other mechanical goods. Typical properties of SBR 1502 are given in the Table 2.2

Table 2.2 Properties of SBR 1502

Bound styrene (%)	23.5
Stabilizer	Non - Staining
Raw MV (ML1+4, 100 °C)	52
Specific gravity	0.94

Resinous filler:

High Styrene Resin (HSR)

High Styrene resin is manufactured by mixing SBR 1502 latex of 23.5% styrene content with high styrene resin latex. It provides high hardness at low specific gravity with superior resistance to abrasion, flex and tear. It can be loaded with a large amount of filler, which helps reduce production cost because it provides the processability in milling, Extrusion and calendaring as a plasticizer at high temperature.

Some of applications of high styrene resin are for shoe soles and heels, rubber hoses, sponges, automobile parts, mechanical goods.

There are lots of grades of HSR in the market. HSR is classified according to the content of styrene in HSR. This is available as resin and resin master batch.

In original formulation (See Table 2.1), HSR 65 % grade was introduced. Properties of HSR 65 % are given in the Table 2.3

Table 2.3 Properties of HSR 65 %

Raw Mooney Viscosity (ML1+4 @100 °C)	61
Bound Styrene (%)	65
Stabilizer	Non- Staining
Specific gravity	1.00

Fibrous filler:

Wood flour

Wood flour is a natural wood fibres and available in various particle sizes. This increases stability of unvulcanised rubber blends and hardness, less shrinkage after vulcanisation, improve the gluing and lacquering specially on ground surfaces. In original formulation (See Table 2.1) wood flour HB 120 grade was employed. HSR 65 % of the wood flour HB 120 are given in the Table 2.4.

Table 2.4 Specifications of wood flour (grade HB 120)

Grain Size (μm)	40-120
Bulk density (g/l)	140-200
PH value	5.5 ± 1

Processing aid

Zewa Harz Pulver

Zewa Harz Pulver is a dark brown powder based on special extract bounded on organic fillers. This is composed of polycondensation product of sulphonated lignin. Typical applications are as activating and dispersing agent mainly for elastomer mixtures based on SBR, NR, NBR, BR and other. Specifications of Zewa Harz Pulver are given in the Table 2.5

Table 2.5 Specifications of Zewa Harz Pulver

Ash (%) -2h @ 850 ° C	5 ± 1
Density (g/l)	1.16 ± 0.02
PH- Value -10 % suspended	7.5 ± 0.5

Aktiplast PP

Aktiplast PP decreases the viscosity of compounds resulting in an easier processing. This leads to high rate of extrusion, better dimensional stability and a constant level of die swell. On the other hand it provides a good dispersion of the fillers and rubber chemicals in the compound. Aktiplast improves scorch behaviour, promotes vulcanisation and makes the process of demoulding much easier, leaving the mould clean. Specifications of the Aktiplast PP are given in the Table 2.6

Table 2.6 Specifications of the Aktiplast PP

Composition	Zinc salts of higher molecular fatty acids
Density (g/cm^3) @ 20 ° C	Approximately 1.08
Ash content (%)	12 – 13
Melting point (° C)	Approximately 97

Coumarone-indene resin (Rhenosin C 90)

This is a polymerisates of carbon-derived unsaturated aromatic C9/C10 hydrocarbons and use as dispersing and tackifying resin for solid rubbers.

Table 2.6 Product descriptions

Softening point (°C) - ASTM-D3461	85-95
Density, (g/ml) @20° C - DIN 51757	1.12- 1.15
Ash (%) - DIN 52005	Max. 0.1