Introduction to Technical Rubber

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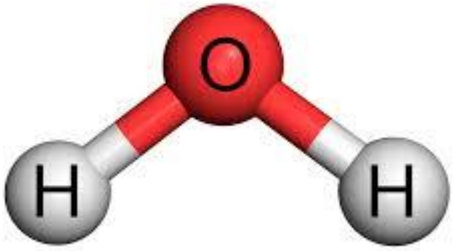
What are polymers?

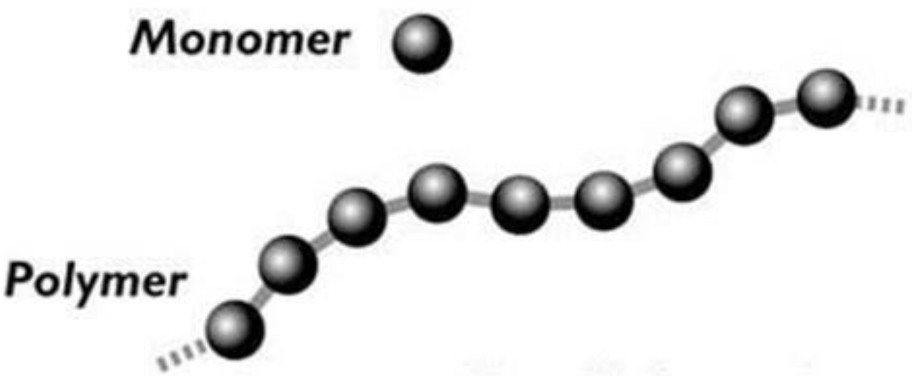
Atoms are the basic building blocks of **matter.**

Atoms combine to make **Molecules,** e.g. a water molecule has two hydrogen atoms and one oxygen atom.



Monomers are molecules that can be bonded to other identical molecules to form a **polymer**.

Polymers can be formed from the same monomer, **homo-polymer,** or from multiple monomors, **ter-polymers** or **co-polymers.**



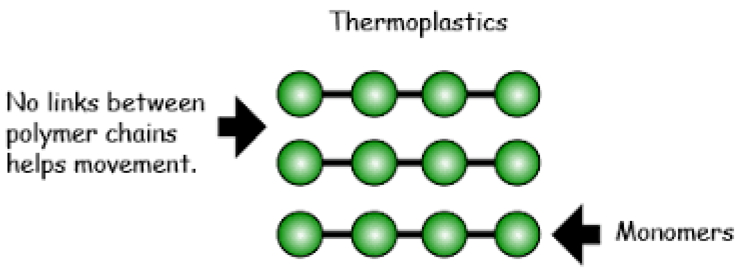
The combination of atoms & molecules and the way in which the long chains or structures tangle and link, results in unique properties.

What are thermoplastics/thermosets?

Unconnected polymer chains slide and move past one another. This means that the materials can be melted, shaped and solidified repeatedly.

These are called **thermoplastic** polymers, and include:

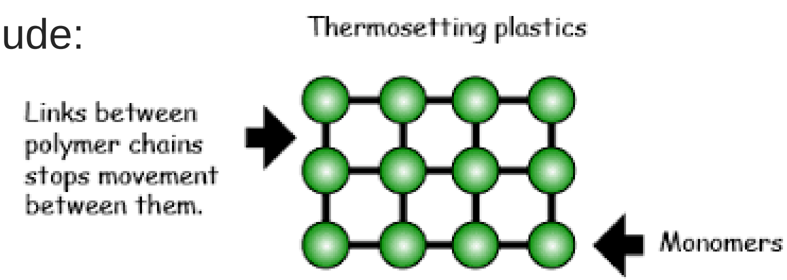
- Polythene (polyethylene) – PE
- Polypropylene – PP
- Polystyrene – PS
- Polyvinylchloride – PVC



The polymer chains can be **crosslinked** using a chemical process called **vulcanisation**. This prevents the material from being repeatedly shaped.

These systems are called thermoset polymers, and include:

- Phenolics
- Melamine
- Epoxides



Thermoplastics can be remelted back into a liquid, thermosets remain in a permanent solid state.

What is rubber?

With a low proportion of crosslinks, the molecular chains can still bend, stretch, & recover.

This results in a thermoset polymer called **rubber.**

Rubber can *creep* and *flow*, but high failure strain can be achieved through vulcanisation.

This enable the rubber to returns to it's original state after being stressed.

Rubber = ***a strong, waterproof, elastic substance made from the juice of a tropical tree or produced chemically.***

History of rubber

Natural rubber comes from the **Hevea Brasiliensis** tree, that grows naturally in South America.

First mentioned by the Spanish explorers in 16th Century, rubber ("**caotchouc**") was used to waterproof locals' clothes and to make shoes, toys, balls etc.

The technology was initially not brought back to Europe.

It was (and still is) tapped from the tree by making an incision in the bark and then collecting the latex in a cup. It is then coagulated.

In the UK during the1820's Mackintosh & Hancock developed the process of mixing rubber.

15 billion kilogrammes of rubber are produced annually, of which two thirds are synthetic.

History of rubber

In the US in 1839, Charles Goodyear adds sulphur to the rubber, making it more stable with a less tacky end product. This was called **vulcanisation** (named after the Roman God of Fire). Volume rubber production then begins through the 1840's.

In the 1880's, seeds are taken from Brazil and cultivated in Kew Gardens (London), before being distributed to British controlled equatorial territories. Malaysia is found to show the greatest success and so plantations are set up with Singapore being the centre for development.

1940's – Synthetic rubbers are developed (including silicone rubbers).

Goodyear struggled to patent vulcanized rubber until 1844.
He died penniless on the 19th July 1860 in New York City.

What is silicone rubber?

Polymers are based on **organic chemistry** with a *carbon-carbon* backbone:

– C – C – C – C – C – C – C – C –

Silicone polymers are different. They are part **inorganic** & based on a *silicone-oxygen* backbone:

– Si – O – Si – O – Si – O – Si – O –

These are called **siloxanes,** a very specialised rubber material, with unique properties.

Silicones (also known as *polysiloxanes*), are polymers that include any inert, synthetic compound made up of repeating units of siloxane.

Silicon (Si) is the 2nd most common element on Earth's surface (28%), after oxygen (46%). Classified as a metalloid, silicon rarely exists in its natural state, and is typically found as compounds with oxygen e.g. sand and quartz.

Silicone = *an elastomer composed of silicon, together with carbon, hydrogen, and oxygen.*

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Types of silicone rubber

Silicone rubber

- **High temperature curing**
  - **Solid silicone (HTV/HCR)**
    - ***Peroxide curing*** — **Free Radical curing**
    - ***Platinum curing*** — **Addition curing**
  - **Liquid silicone (LSR)**
    - ***Platinum curing*** — **Addition curing**
- **Room temperature curing**
  - **Two component RTV2**
    - Platinum-catalysed — *Addition curing*
    - Zinc-catalysed — *Condensation cure*
  - **One component RTV1**
    - Platinum-catalysed — *Addition curing*
    - Zinc-catalysed — *Condensation cure*

Silicone rubber can be found in a very wide range of products, including aerospace; automotive; cooking; clothing; electronics; medical devices.

Why use technical rubber?

Because it can resist.

- Temperature extremes
- Water
- Condensate
- Fire
- Chemicals
- Gases
- Fuels

Which reduces risk.

Engineers must trust the material.

Technical rubber groups

- Commodity elastomers
- High performance elastomers
- Speciality materials

Global growth in demand for technical rubber

Technical rubber groups

- Commodity Elastomers
  - Natural rubber (NR)
  - Styrene butadiene rubber (SBR)
  - Polychloroprene (CR)
  - EPDM / EPR rubber
  - Nitrile rubber - High, Medium, Low (NBR)
- High performance elastomers
- Speciality materials

Elastomers in widespread use

Technical rubber groups

- Commodity Elastomers
- High performance elastomers
  - Methyl Vinyl Silicone (VMQ)
  - Phenyl Silicone (PVMQ)
  - Fluorosilicone (FVMQ)
  - Fluorocarbon & derivatives (FKM)
  - Hydrogenated Nitrile (HNBR)
- Speciality materials

Materials that outperform other grades

Technical rubber groups

- Commodity Elastomers
- High performance elastomers
- Speciality materials
  - Hypalon® (CSM)
  - Vamac® (Ethylene Acrylic) (AEM)
  - Polyacrylic (ACM)
  - Carboxylated NBR (XNBR)
  - Butyl Rubber (IIR)
  - Epichlorohydrin (ECO)

Low volume grades with unique properties

Common technical rubbers: Properties

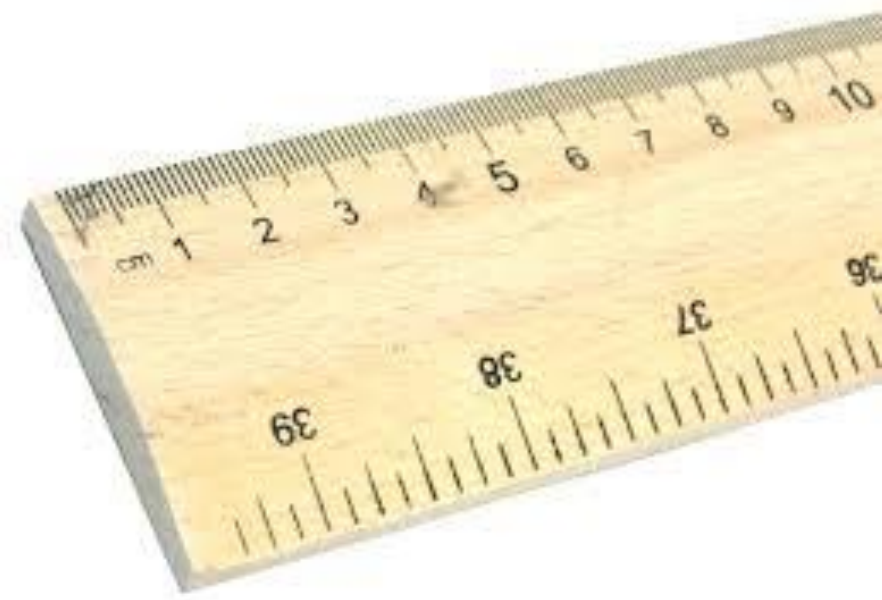
	Natural Rubber	SBR	NBR	EPDM	Silicone	HNBR	FKM	Fluorosilicone
Cost factor	1	1	2	2	5	10	15	17
Max continuous temperature °C	75	85	100	150	250	150	250	200
Max intermittent temperature °C	105	115	130	160	315	160	300	250
Low temperature °C	-60	-50	-20	-50	-60	-20	-20	-60
Heat aging resistance	Fair	Fair	Fair	Good	Excellent	Good	Very good	Very good
Hardness range	30-95	40-90	40-90	30-85	5-90	40-90	50-90	20-90
Physical strength	Excellent	Good	Good	Good	Fair	Very good	Good	Poor
Tear resistance	Excellent	Fair	Good	Good	Fair	Good	Very good	Fair
Compression set	Good	Good	Good	Good	Good	Good	Good	Poor
Resilience	Excellent	Good	Good	Very good	Good	Good	Fair	Good
Colourability	Good	Good	Poor	Poor	Excellent	Good	Poor	Good

Common technical rubbers: Resistance

	Natural Rubber	SBR	NBR	EPDM	Silicone	HNBR	FKM	Fluorosilicone
Cost factor	1	1	2	2	5	10	15	17
Abrasion resistance	Excellent	Excellent	Excellent	Very good	Poor	Excellent	Good	Poor
Water resistance	Very good	Good	Good	Excellent	Very good	Good	Good	Very good
UV resistance	Fair	Good	Fair	Good	Very good	Good	Good	Very good
Ozone resistance	Poor	Poor	Poor	Outstanding	Excellent	Good	Outstanding	Excellent
Oxygen resistance	Good	Good	Fair	Excellent	Excellent	Good	Outstanding	Excellent
Weathering	Fair	Fair	Good	Outstanding	Excellent	Very good	Excellent	Excellent
Electrical properties	Very good	Very good	Poor	Very good	Excellent	Poor	Good	Excellent
Flame resistance	Poor	Poor	Poor	Poor	Excellent	Poor	Excellent	Excellent
ASTM Oil 1 @ 100C	Poor	Poor	Good	Poor	Good	Good	Excellent	Very good
ASTM Oil 3 @ 100C	Poor	Poor	Good	Poor	Fair	Good	Excellent	Good
ASTM Fuel B @ 40C	Poor	Poor	Fair	Good	Poor	Fair	Excellent	Fair
Alcohol resistance	Good	Good	Good	Good	Good	Good	Good	Good
Acetone resistance	Fair	Fair	Poor	Good	Poor	Poor	Poor	Poor
Benzene resistance	Poor	Poor	Poor	Poor	Poor	Poor	Poor	Poor
Acid resistance	Fair	Fair	Good	Good	Fair	Good	Excellent	Good
Base resistance	Good	Good	Fair	Good	Fair	Fair	Good	Fair
Gas permeability	Good	Fair	Very good	Fair	Very good	Good	Good	Poor

Measuring technical rubber characteristics

- Hardness
- Specific gravity
- Rheometry
- Viscosity
- Mechanical properties
- Tear strength
- Compression set



Tests can be carried out on cured, or un-cured rubber.

Measuring technical rubber characteristics

- Hardness
    - Defined as a material's resistance to indentation, hardness is determined using a **durometer**. The higher the number, the harder the material.
    - Other Shore scales may occasionally be used, along with other test methods, such as IRHD (International Rubber Hardness Degrees).
- Specific gravity
- Rheometry
- Viscosity
- Mechanical properties
- Tear strength
- Compression set

ISO7619-1

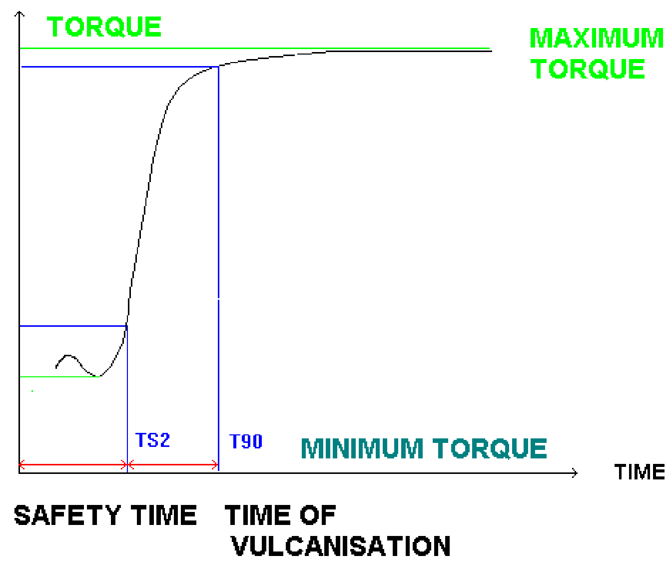
Measuring technical rubber characteristics

- Hardness
- Specific gravity
  - The ratio of the density of a substance to the density of a reference substance.
  - Dividing the mass of the object by the mass of water is commonly used.
- Rheometry
- Viscosity
- Mechanical properties
- Tear strength
- Compression set

ISO 2781

Measuring technical rubber characteristics

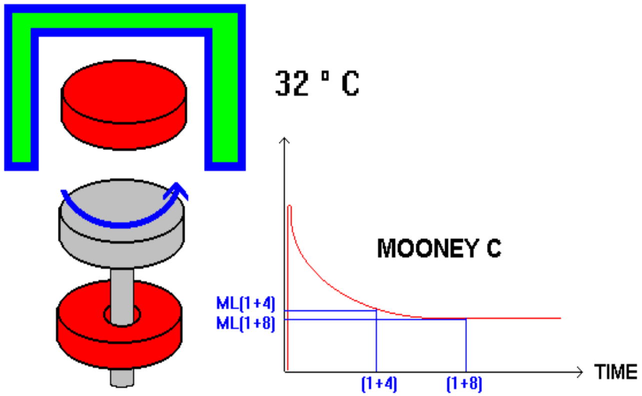
- Hardness
- Specific gravity
- Rheometry
    - A rheometer is a device used to measure the way in which a polymer flows in response to applied forces.
    - Useful for those materials (such as rubber) which cannot be defined by a single value of viscosity and therefore require more parameters to be set and measured than is the case for a viscometer.
- Viscosity
- Mechanical properties
- Tear strength
- Compression set



ISO 3417

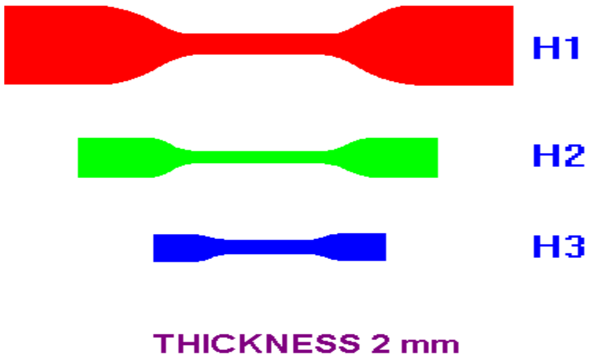
Measuring technical rubber characteristics

- Hardness
- Specific gravity
- Rheometry
- Viscosity
  - Measured using a Mooney viscometer, which contains a rotating spindle & heated dies
  - The rubber encloses and overflows the spindle and the Mooney viscosity is calculated from the torque on the spindle.
- Mechanical properties
- Tear strength
- Compression set



ISO 289-1

Measuring technical rubber characteristics



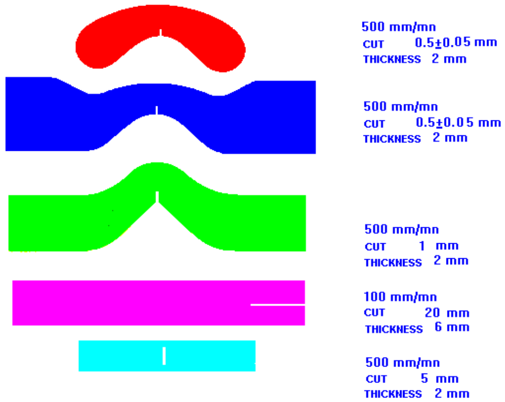
- Hardness
- Specific gravity
- Rheometry
- Viscosity
- Mechanical properties
  - **Tensile strength:** the resistance of a material to breaking under tension
  - **Elongation @ break**: the ratio between changed length and initial length after breakage of the test specimen - expressing the capability of a material to resist changes of shape without crack formation
  - **Modulus:** a measurement of stiffness

  All are performed on a **Tensometer** or **UTM** (Universal Testing Machine).
- Tear strength
- Compression set

ISO 37

Measuring technical rubber characteristics

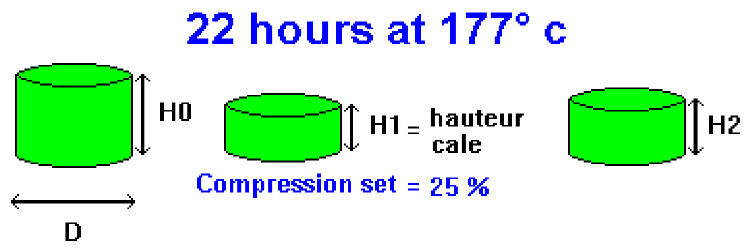
- Hardness
- Specific gravity
- Rheometry
- Viscosity
- Mechanical properties
- Tear strength
    - The tensile force required to rupture a pre-slit sample under controlled conditions.
    - The form of the sample and the pre-split or notched rupture can vary in size, depending on the test method being performed.
- Compression set



ISO 34

Measuring technical rubber characteristics

- Hardness
- Specific gravity
- Rheometry
- Viscosity
- Mechanical properties
- Tear strength
- Compression set
    - The permanent deformation remaining when a force (that was applied to it) is removed.
    - An effective method of determining sealing characteristics.



$$CS = \frac{(H0 - H2) \times 100}{(H0 - H1)}$$

ISO 815-1

Measuring technical rubber characteristics

- Hardness
- Specific gravity
- Rheometry
- Viscosity
- Mechanical properties
- Tear strength
- Compression set
- Other tests
    - Rebound resilience
    - Immersion / volume swell tests
    - Abrasion tests
    - Aging tests
    - Soxhlet extraction tests
    - TGA (thermal gravimetrical analysis)
    - FTIR (fourier-transform infrared spectroscopy)

Technical rubber approvals

		EPDM 60 (peroxide)	EPDM 70 (peroxide)	EPDM 60 (suphur)	EPDM 70 (suphur)	FKM 50 Terpolymer	FKM 70 Terpolymer	VMQ 40	VMQ 60	HNBR 60	NBR 45 (suphur)	NBR 60 (suphur)
EN14241-1	*Tested & Approved:*	✓							✓			
	Designed to meet:		✓	✓	✓	✓	✓	✓				
T120 W2 K2 LI	*Tested & Approved:*	✓										
	Designed to meet:		✓			✓	✓	✓				
T80 W2 K2 LI	*Designed to meet:*			✓	✓							
T120 W1 K2 LI	*Tested & Approved:*								✓			
	Designed to meet:							✓				
EN549 H1 E2	*Tested & Approved:*							✓				
	Designed to meet:											
EN549 H2 E2	*Tested & Approved:*								✓			
	Designed to meet:											
EN549 H2 B2	*Tested & Approved:*										✓	✓
	Designed to meet:											
EN549 H2 C1	*Tested & Approved:*									✓		
	Designed to meet:											
EN549 H2 E1	*Tested & Approved:*					✓						
	Designed to meet:											
EN549 H3 E1	*Tested & Approved:*						✓					
	Designed to meet:											

Materials may be designed to meet specific standards

Technical rubber applications

	EPDM 60 (peroxide)	EPDM 70 (peroxide)	EPDM 60 (sulphur)	EPDM 70 (sulphur)	FKM 50 Terpolymer	FKM 70 Terpolymer	VMQ 40	VMQ 60	HNBR 60	NBR 45 (sulphur)	NBR 60 (sulphur)
Gaskets	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Seals	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Grommets	✓	✓	✓	✓			✓	✓	✓	✓	✓
Burner grommets					✓	✓					
O-rings	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Caps	✓	✓	✓	✓			✓	✓			
Valves	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Tubes							✓	✓			
Profiles							✓	✓			
Sheeting							✓	✓			
Gas tubes / hoses									✓		
Condensate tubes / hoses	✓	✓	✓	✓							
Comments:							*WRAS compliant grades available (20 – 90 Shore A)*				

Custom materials can be developed to satisfy most applications

Material design criteria

- Temperature - Effect of chemicals at elevated temp.
- Conditions - Dynamic vs. Static
- Pressures - Compatibility with surrounding materials
- Polymer grade - Specific formulations
- Suitability/compatibility for processing method
- Quality planning – FMEA, FEA, PPAP

Understanding requirements at the outset is crucial

Additives

Processing Additives

- Plasticisers - for control of plasticity and crepe hardening
- Handling Additives - for modification of green strength
- Mould Release Additives – for easier de-moulding

Performance Additives

- Fire / Flame Retardants
- Heat Stability Additives
- Acid Acceptors – to reduce ‘bloom’ & improve compression set
- Oil Resistance Additives
- Glass Spheres – to reduce density

There are countless other additives to achieve distinct properties.
e.g. Thermal conductivity, electrical conductivity, etc.

Economics of material selection

- Value in Use – High initial price may be reclaimed over reduced service intervals and maintenance / warranties
- Reducing cost / increasing performance
- Rationalisation / Standardisation of material selection

The cheapest material may not be the best solution

How is silicone rubber processed?

- Compression moulding
- Injection moulding
- Liquid silicone (LSR) injection moulding
- Extrusion
- Cleanroom manufacture

Dependent on volumes, required quality, and tooling budget.

Processing: Compression moulding

- Compression moulding
  - Perfect for low volumes and prototypes
  - Bonding to other materials
  - Lower price tooling
  - Not cost effective for very high volumes
- Injection moulding
- Liquid silicone (LSR) injection moulding
- Extrusion
- Cleanroom manufacture

Relatively low cost for good quality components.

Processing: Injection moulding

- Compression moulding
- Injection moulding
    - Cost effective for high volumes
    - Bonding to other materials
    - Requires specialist tool design
- Liquid silicone (LSR) injection moulding
- Extrusion
- Cleanroom manufacture

Enables flexible volumes but longer tooling lead times.

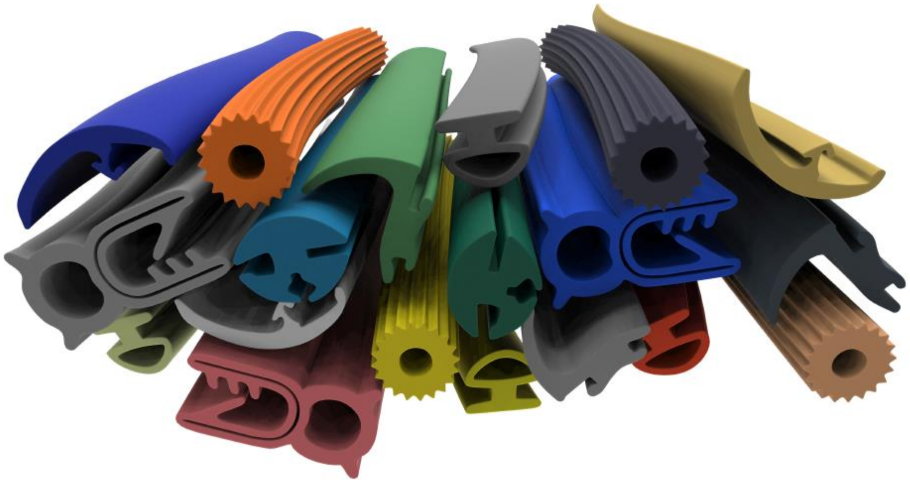
Processing: LSR moulding

- Compression moulding
- Injection moulding
- Liquid silicone (LSR) injection moulding
  - Essential for ultra high volumes
  - Frequently automated
  - Expensive tool design and manufacture
- Extrusion
- Cleanroom manufacture

Perfect for very high volumes and intricate components.

Processing: Extrusion

- Compression moulding
- Injection moulding
- Liquid silicone (LSR) injection moulding
- Extrusion
    - Tubes, profiles, cord, & tape
    - Often cut, joined, &/or punched
    - Low cost tooling
- Cleanroom manufacture



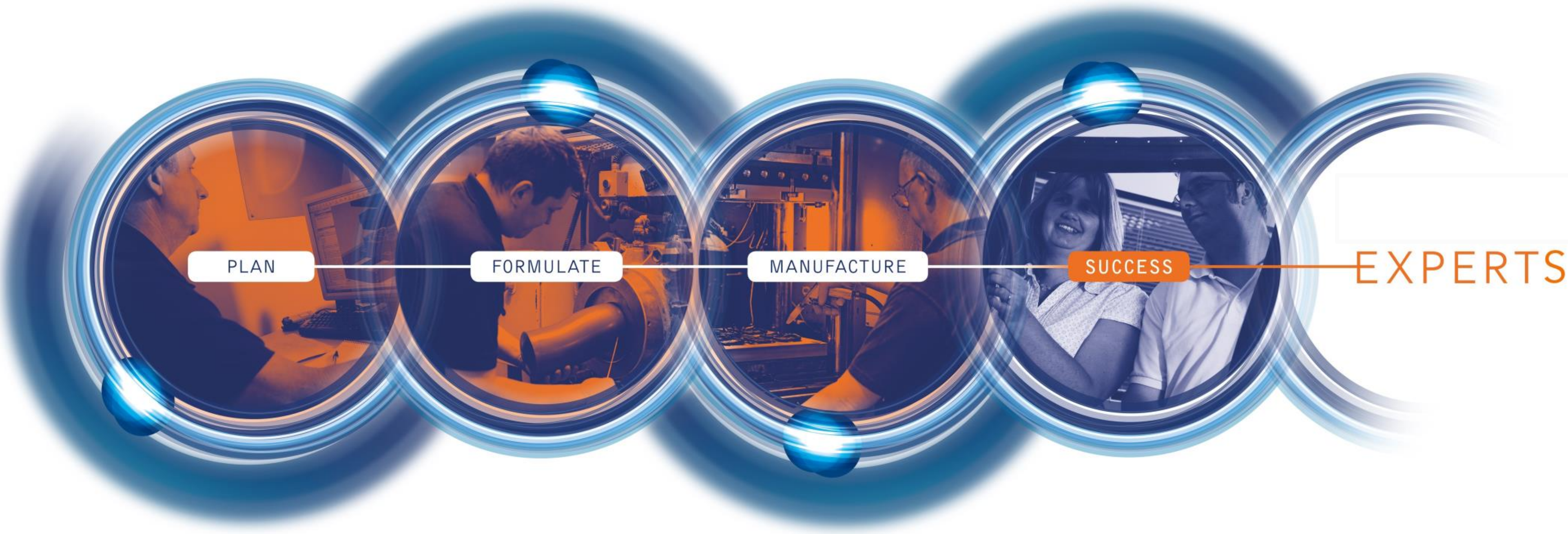
Extensive processing experience required for producing tools.

Processing: Cleanroom manufacture

- Compression moulding
- Injection moulding
- Liquid silicone (LSR) injection moulding
- Extrusion
- Cleanroom manufacture
    - Contamination controlled
    - Moulding & extrusion
    - Assembly and packing

Not just for medical – increasingly used for electronics.

Primasil. The technical rubber experts.



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