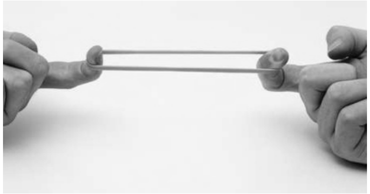
ELASTOMER TECHNOLOGY

History, Compounding and Processing

Elastomer

"High molar mass material which when deformed at room temperature reverts quickly to nearly original size and form when the load causing the deformation has been removed"



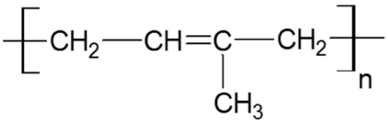
Elastomer and Rubber

- Originally, "rubber" referred to a naturally derived (organic) material. The term was first used by an English chemist (Joseph Priestley). Joseph was working with natural rubber and observed that it could "rub out" a pencil mark.
- In the past, "rubber" was used to describe materials that occurred naturally in nature; and "elastomer" was used for materials that were produced synthetically.
- An elastomer is a polymer that shows elastic properties. The terms rubber-like and elastomeric mean almost the same thing, the terms "rubber" and "elastomer" are often used interchangeably today.

Natural Rubber

- Natural rubber is tapped from rubber trees (*Hevea brasiliensis*) as latex
- In Southeast Asia and other parts of the world

- Latex is a colloidal dispersion of solid particles of the polymer *polyisoprene* in water.
- The molecular weights of rubber molecules range from 50,000 to 3,000,000 Da.

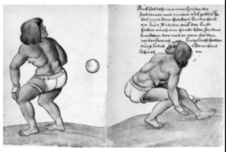


$$\left[CH_2-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_2 \right]_n$$

History of Rubber

- **First millennium BC – Mexico**
  - First evidence of the Mesoamerican ballgame
- **6th century – Mexico and Central America – Aztecs/Mayans**
  - Balls
  - Dipped feet to make shoes
  - Coated Fabrics

- In 1490, Columbus supposedly watched a Mesoamerican ballgame.



- In 1770, the famous chemist Priestley discovered that rubber could be used for removing pencil marks.

- In 1823, Charles Macintosh discovered that rubber was soluble in hexane.
- Further, when the solution was applied to clothing, a thin layer was left on the clothes.
- He invented the "Macintosh" (a raincoat -- not a computer).

CHAS. MACINTOSH & CO.
PATENTEES
OF
Indian Rubber
WATER-PROOF CLOTHS,
OF
DOUBLE TEXTURE.
AIR CUSHIONS, PILLOWS, &c.
46, CHEAPSIDE,
AND 58, CHARING CROSS, LONDON.
And at the Manufactory, Manchester.

CAUTION.

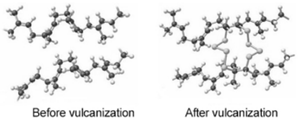
CHAS. MACINTOSH & Co. having ascertained that spurious Articles have been sold as IMPROVED MACINTOSH GARMENTS, think it due to the Public and themselves to state, that none are genuine which have not the Autograph *C. Macintosh & Co.* engraved with the Royal Arms on the lining, as they send out none without this stamp.

(See Vignette, and 58, in the Engraving.)

PATENTEES OF INDIAN RUBBER WATER PROOF CLOTHS, OF DOUBLE TEXTURE, AIR CUSHIONS, PILLOWS &c.
58, CHARING CROSS & 46, CHEAPSIDE, LONDON.

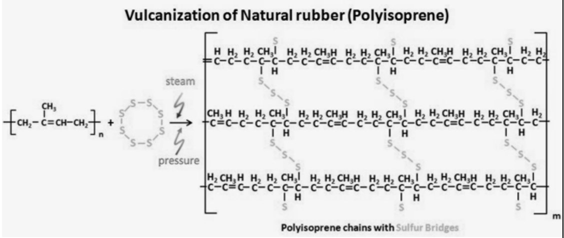
- In cold weather, they cracked.
- In hot weather, two people with Macintoshes often became inseparable. Their coats stuck together.

- In 1839, Charles Goodyear heated the raw rubber-sulfur-lead combination by chance and discovered how to vulcanize rubber and make it non-sticky and much more usable.



- In 1843 Hancock combined sulfur with rubber and heat and coined the term vulcanization from the god Vulcan of Roman mythology.

In this process, because of added sulfur, the rubber becomes cross linked and also has better elasticity.



- In 1889, Dunlop invented the first commercially successful pneumatic tire in England.
- Dunlop produced his first vehicle tire in 1906.
- In 1904, Stern blended carbon black with rubber.

Synthetic Rubber

The period between World Wars I and II witnessed the first development of a true synthetic substitute for natural rubber;

1910-1940: Russia

- Lebedev, a Russian chemist, was the first to polymerize butadiene.
- In 1928, he developed a method for producing polybutadiene using sodium as a catalyst.
- In 1936 the Soviet Union built the world's first polybutadiene plant.

1930s: Germany

- In Germany, scientists from Bayer (IG Farben) reproduced Lebedev's processes and used the trade name Buna, derived from Bu for butadiene, Na for sodium.
- Then Germans developed the emulsion copolymerisation of butadiene- styrene (Buna S).
- Polyisobutylene (PIB) was first developed by BASF in 1931.
- In 1937, the production of Buna-N (nitrile butadiene rubber, NBR), an oil resistant rubber was started.

other significant materials:

- In 1930s, Dupont developed Neoprene (polychloroprene,chloroprene rubber, CR) in the US.
- Butyl rubber (IIR, isobutylene isoprene copolymer) was developed in the 1940s.
- Production of styrene-butadiene rubber (SBR), then called GR-S, began in a US government plant in 1942.
- EPDM rubber is developed in 1960s as a terpolymer of ethylene, propylene, and a diene-component.

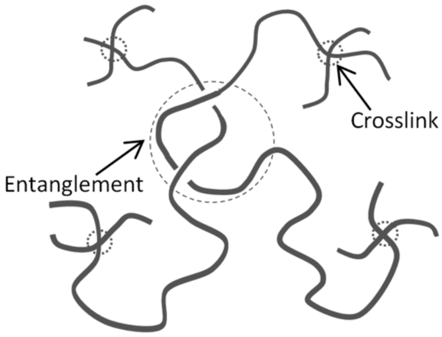
- The advent of World War II highlighted the importance of rubber as a raw material.
- Wide variety of synthetic rubbers have since been developed, and in the early 1960s production of natural rubber was surpassed by that of synthetic elastomers.
- By 1990, two-thirds of world rubber production consisted of synthetic varieties.

Fundamental Properties of Elastomers

- The chains can typically consist of 300,000 or more monomer units.
- They can be composed of repeated units of the same monomer, or made up of two or more different monomers.
- Elasticity & Resilience

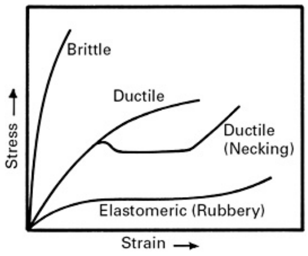
Elasticity

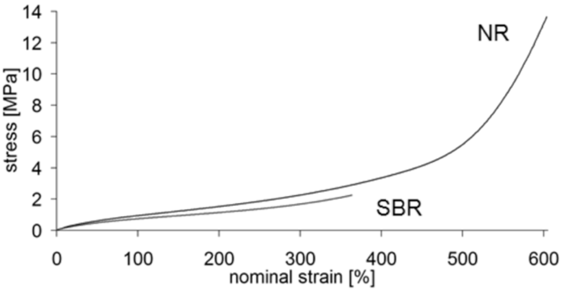
- Elasticity is the ability of a material to return to its original shape and size after being stretched, compressed, twisted or bent.
- Elastic deformation (change of shape or size) lasts only as long as a deforming force is applied, and disappears once the force is removed.



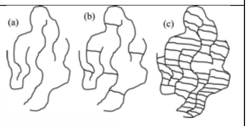
Resilience

- Resilience as applied to elastomers is essentially their ability to return quickly to their original shape after temporary deflection.
- In other words, it indicates the speed of recovery, unlike compression set, which indicates the degree of recovery.





Crosslink density



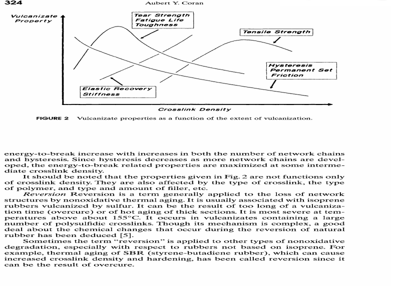

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FIGURE 2 Vulcanizate properties as a function of the extent of vulcanization.

energy-to-break increase with increases in both the number of network chains and hysteresis. Since hysteresis decreases as more network chains are developed, the energy-to-break related properties are maximized at some intermediate crosslink density.

It should be noted that the properties given in Fig. 2 are not functions only of crosslink density. They are also affected by the type of crosslink, the type of polymer, and type and amount of filler, etc.

Reversion Reversion is a term generally applied to the loss of network structures by nonoxidative thermal aging. It is usually associated with isoprene rubbers vulcanized by sulfur. It can be the result of too long of a vulcanization time (overcure) or of hot aging of thick sections. It is most severe at temperatures above about 155°C. It occurs in vulcanizates containing a large number of polysulfidic crosslinks. Though its mechanism is complex, a good deal about the chemical changes that occur during the reversion of natural rubber has been deduced [5].

Sometimes the term "reversion" is applied to other types of nonoxidative degradation, especially with respect to rubbers not based on isoprene. For example, thermal aging of SBR (styrene-butadiene rubber), which can cause increased crosslink density and hardening, has been called reversion since it can be the result of overcure.

Most elastomers possess a number of other useful properties, such as:

- Low permeability to air, gases, water and steam
- Good electrical and thermal insulation
- Good mechanical properties
- The ability to adhere to various fibres, metals and rigid plastics.

- Most types of elastomers are **thermosets,** which gain most of their strength after vulcanization – an irreversible cross-linking of their polymer chains that occurs when the compound is subjected to pressure and heat.

- **Thermoplastic** elastomers, on the other hand, have weaker cross-linking and can be moulded, extruded and reused like plastic materials, while still having the typical elastic properties of elastomers.

RUBBER PROCESSING TECHNOLOGY

Overview of Rubber Processing

- Many of the production methods used for plastics are also applicable to rubbers
- However, rubber processing technology is different in certain respects, and separate from the plastics industry.
- The rubber industry and goods made of rubber are dominated by one product: tires
  - Tires are used in large numbers on automobiles, trucks, aircraft, and bicycles

Two Basic Steps in Rubber Goods Production

1. Production of the rubber itself
   - Natural rubber (NR) is an agricultural crop
   - Synthetic rubbers is based on petroleum
2. Processing into finished goods:
   - Compounding
   - Mixing
   - Shaping
   - Vulcanizing

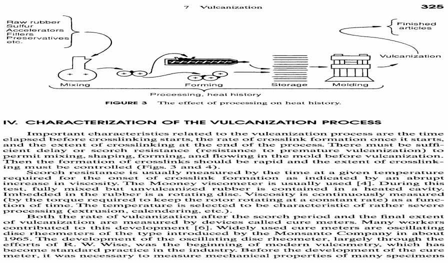

7 Vulcanization **325**

FIGURE 3 The effect of processing on heat history.

IV. CHARACTERIZATION OF THE VULCANIZATION PROCESS

Important characteristics related to the vulcanization process are the time elapsed before crosslinking starts, the rate of crosslink formation once it starts, and the extent of crosslinking at the end of the process. There must be sufficient delay or scorch resistance (resistance to premature vulcanization) to permit mixing, shaping, forming, and flowing in the mold before vulcanization. Then the formation of crosslinks should be rapid and the extent of crosslinking must be controlled (Figs. 3 and 4).

Scorch resistance is usually measured by the time at a given temperature required for the onset of crosslink formation as indicated by an abrupt increase in viscosity. The Mooney viscometer is usually used [4]. During this test, fully mixed but unvulcanized rubber is contained in a heated cavity. Imbedded in the rubber is a rotating disc. Viscosity is continuously measured (by the torque required to keep the rotor rotating at a constant rate) as a function of time. The temperature is selected to be characteristic of rather severe processing (extrusion, calendering, etc.).

Both the rate of vulcanization after the scorch period and the final extent of vulcanization are measured by devices called cure meters. Many workers contributed to this development [6]. Widely used cure meters are oscillating disc rheometers of the type introduced by the Monsanto Company in about 1965. The development of the oscillating disc rheometer, largely through the efforts of R. W. Wise, was the beginning of modern vulcometry, which has become standard practice in the industry. Before the development of the cure meter, it was necessary to measure mechanical properties of many specimens

The Rubber Industries

- Production of raw NR is **an agricultural industry** because *latex*, the starting ingredient, is grown on plantations in tropical climates
- By contrast, synthetic rubbers are produced by the **petrochemical industry**
- Finally, processing into tires and other products occurs at processor (fabricator) plants, commonly known as the **rubber industry**

Production of Natural Rubber

- Natural rubber is tapped from rubber trees (*Hevea brasiliensis*) as latex
  - In Southeast Asia and other parts of the world
- Latex is a colloidal dispersion of solid particles of the polymer *polyisoprene* in water
  - Polyisoprene $(C_5H_8)_n$ is the chemical substance that comprises NR, and its content in the emulsion is about 30%

Recovering the Rubber

- Preferred method to recover rubber from latex involves coagulation - adding an acid such as formic acid (HCOOH)
  - Coagulation takes about 12 hours
- The coagulum, now soft solid slabs, is then squeezed through rolls which drive out most of the water and reduce thickness to about 3 mm.
- The sheets are then draped over wooden frames and dried in smokehouses for several days

Dried rubber sheets

Rubber bales

Grades of Natural Rubber

- The resulting rubber, now in a form called *ribbed smoked sheet*, is folded into large bales for shipment to the processor
- In some cases, the sheets are dried in hot air rather than smokehouses, and the term *air-dried sheet* is used
  - This is considered a better grade of rubber
- A still better grade, called *pale crepe* rubber, involves two coagulation steps, followed by warm air drying

Natural rubber properties include:

- Ease of processing
- Excellent dynamic performance
- Limited high temperature resistance (max. +70C)
- Good low temperature properties (-50C)
- Ability to bond strongly with metal parts
- High resistance to tear and abrasion, can be self-healing
- Poor resistance to sunlight, oxygen, ozone, solvents and oils.

Natural rubber has the following advantages over synthetic rubber:

- Good dynamic performance
- Low level of damping
- Excellent resistance to heat buildup during flexing
- Greater resistance to tearing when hot.

Synthetic Rubber

- Most synthetic rubbers are produced from petroleum by the same polymerization techniques used to synthesize other polymers
- Synthetic rubbers are supplied to rubber processors in the form of large bales
- The rubber industry has a long tradition of handling NR in these unit loads

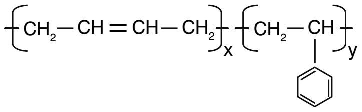
Synthetic rubber can have the following advantages over natural rubber:

- Applying polymer chemistry techniques allow greater opportunities for customization of properties
- More resistant to oil, certain chemicals and oxygen
- Better aging and weathering resistance
- Resilience over a wider temperature range

The major classes of synthetic rubber are:

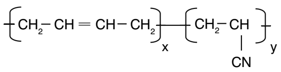
- Styrene-butadiene copolymer (SBR)
- Nitrile elastomers (poly (butadiene-acrylonitrile) NBR rubbers / HNBR
- Butyl rubbers (IIR)
- Neoprene (polychloroprene) (CR)
- Ethylene-propylene rubbers (EPDM)
- Urethane elastomers (EU)
- Silicone rubbers VMQ)
- Fluoroelastomer (FKM)

Styrene butadiene (SBR)



Needs reinforcing fillers for high strength, when it has similar chemical and physical properties to natural rubber, with generally better abrasion resistance but poorer fatigue resistance. Widely used in car and light vehicle tyres. Also conveyor belts, moulded rubber goods, shoe soles and roll coverings.

Nitrile (NBR)



$$\left[CH_2-CH=CH-CH_2\right]_x\left[CH_2-\underset{CN}{\underset{|}{CH}}\right]_y$$

Good aliphatic hydrocarbon oil/fuel resistance and resilience. Limited weathering resistance and only modest temperature resistance. Typical temperature range: -30°C to +120°C (-22°F to +248°F). Widely used in sealing applications. Low temperature grades available down to -50°C (-58°F). As with hydrogenated nitrile, many properties can be influenced by varying its acrylonitrile to butadiene ratio.

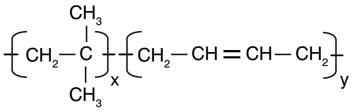
Butadiene (BR) (polybutadiene)

$$\left[CH_2-CH=CH-CH_2\right]_n$$

Widely used in blends with natural rubber and styrene butadiene rubber for tyres, where it reduces heat build-up and improves abrasion resistance. Low hysteresis, good flexibility at low temperatures, high abrasion resistance in severe conditions. Also used in shoes, conveyor and transmission belts.

Butyl (IIR)

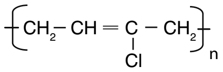
(isobutylene-isoprene copolymer)



$$-\left[CH_2-\underset{CH_3}{\overset{CH_3}{C}} \right]_x-\left[CH_2-CH=CH-CH_2 \right]_y-$$

Low permeability to gases and hence used for inner tubes. High damping at ambient temperatures. Good ozone, weathering, heat and chemical resistance but not oil resistant. Other uses include wire and cable applications, pharmaceutical closures and vibration isolation.

Chloroprene (CR)

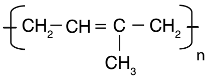


$$-\left[CH_2-CH=\underset{Cl}{C}-CH_2 \right]_n-$$

Good weather and ozone resistance, and fair resistance to inorganics. Resistant to many chlorofluorocarbons. Low cost. Moderate oil resistance and limited temperature resistance. Typical temperature range: -40°C to +120°C (-40°F to +248°F). Useful in pneumatic applications.

Isoprene (IR)

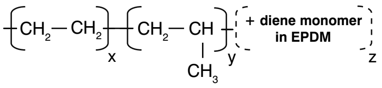
(synthetic cis-polyisoprene)



$$-\left[CH_2-CH=\underset{CH_3}{C}-CH_2 \right]_n-$$

Similar chemical structure to natural rubber, but less easy to process and can have lower tensile and tear strength. Its relative purity provides better performance at lower temperatures. Can be used interchangeably with natural rubber in all but the most demanding applications.

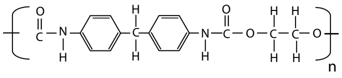
Ethylene propylene (EPM/EPDM)



$$-\left[CH_2-CH_2 \right]_x-\left[CH_2-\underset{CH_3}{CH} \right]_y-\left[\text{+ diene monomer in EPDM} \right]_z$$

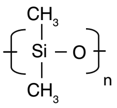
Excellent ozone/weathering resistance; excellent hot water and steam resistance; good resistance to inorganic and polar organic chemicals. Low resistance to hydrocarbons. Typical temperature range: -45°C to +150°C (-49°F to +302°F), up to +180°C (+356°F) in steam. Mineral oil/grease lubricants should not be used to aid assembly.

Polyurethane (AU, EU)



Very versatile, with good abrasion resistance, high tensile and tear strength, good resistance to aliphatic solvents and mineral oils, oxygen and ozone. Can be formulated to have high modulus with a high filler content. Poor heat resistance and can have poor creep resistance, particularly in moist conditions. Uses in seals, metal forming dies, liners, rollers, wheels, conveyor belts, etc.

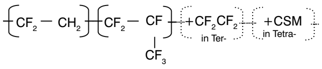
Silicone (Q)



$$-\left[\underset{CH_3}{\overset{CH_3}{Si}}-O \right]_n-$$

Only moderate physical properties but capable of retaining them over a very wide temperature range. Some types are affected by moisture. Good electrical resistance properties. Readily available in liquid form (LSR). Widely used in sectors such as pharmaceutical, medical, wire and cable, automotive and aerospace.

Fluorocarbon (FKM)



$$-\!\left[CF_2-CH_2\right]\!-\!\left[CF_2-\underset{\displaystyle CF_3}{\underset{|}{CF}}\right]\!-\!\underset{\text{in Ter-}}{\left[+CF_2CF_2\right]}\!-\!\underset{\text{in Tetra-}}{\left[+CSM\right]}\!-$$

Excellent ozone/weathering resistance; good heat resistance. Limited resistance to steam, hot water and other polar fluids (except Tetra-) although new peroxide cured grades with no metal oxides are better. Attacked by amines, limited low temperature capabilities (except specialised grades). Typical temperature range: -20°C to +230°C (-4°F to +446°F). Properties vary significantly with type.

Compounding

The basic properties of elastomers are highly dependent on the polymers used in their manufacture.

- The factors that affect the quality of the resulting elastomer include
  - the quality of the raw ingredients,
  - the style of mixer and
  - the quality control in mixing
  - processing of the compounded material

Ingredients

Ingredients:

- Polymers
- Curatives
- Fillers
- Accelerators
- Activators
- Pigments
- Flame retardants

Ingredients:

- Retarders
- Protectants/ antidegradants
- Process aids
- Coupling agents
- Co-agents
- Odorants and deodorants

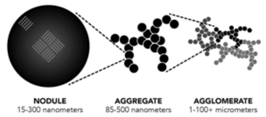
Polymers

- The polymer, or blend of polymers, is the fundamental component
- Optimization of
  - service performance
  - processing requirements
  - cost
- Very high molecular weight polymers can for example produce extremely tough materials with poor flow.

Fillers

- Fillers are added primarily to provide reinforcement and secondly to reduce cost.
- Two basic categories:
  - Reinforcing or semi-reinforcing,
  - Diluent (non-reinforcing, for cheapening).

- The most popular reinforcing and semi-reinforcing fillers are carbon blacks
- They become more reinforcing as particle size decreases.
- Highly reinforcing fillers can make a compound tough, which can result in poor flow.
- Carbon blacks are alkaline in nature and tend to accelerate cure.



- Non-black filllers tend to be acidic.
- They can retard cure as well as absorb moisture, which can result in blistering problems during the processing stage.

- Diluent, or non-reinforcing, fillers have a large particle size and do not 'bond' to the polymer.
- They are mainly added to reduce cost.
- Examples include soft clay, calcium carbonate, and talc.

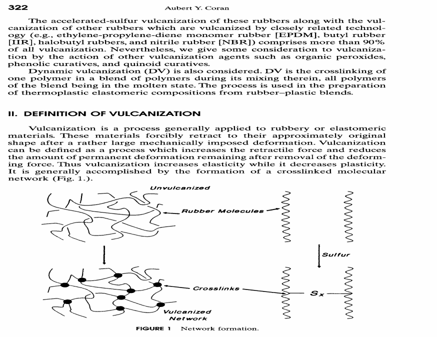
Curatives ➔ What is Vulcanization?

- The treatment that accomplishes cross-linking of elastomer molecules
- Makes the rubber stiffer and stronger but retain extensibility
- The long-chain molecules become joined at certain tie points, which reduces the ability to flow
  - Soft rubber has 1 or 2 cross-links per 1000 mers
  - As the number of cross-links increases, the polymer becomes stiffer (e.g., hard rubber)

Curatives ➔ What is Vulcanization?

- Vulcanization can be defined as a process which increases the retractile force and reduces the amount of permanent deformation remaining after removal of the deforming force.

- Thus vulcanization increases elasticity while it decreases plasticity.



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The accelerated-sulfur vulcanization of these rubbers along with the vulcanization of other rubbers which are vulcanized by closely related technology (e.g., ethylene-propylene-diene monomer rubber [EPDM], butyl rubber [IIR], halobutyl rubbers, and nitrile rubber [NBR]) comprises more than 90% of all vulcanization. Nevertheless, we give some consideration to vulcanization by the action of other vulcanization agents such as organic peroxides, phenolic curatives, and quinoid curatives.

Dynamic vulcanization (DV) is also considered. DV is the crosslinking of one polymer in a blend of polymers during its mixing therein, all polymers of the blend being in the molten state. The process is used in the preparation of thermoplastic elastomeric compositions from rubber–plastic blends.

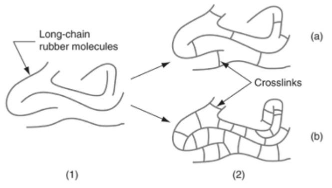
II. DEFINITION OF VULCANIZATION

Vulcanization is a process generally applied to rubbery or elastomeric materials. These materials forcibly retract to their approximately original shape after a rather large mechanically imposed deformation. Vulcanization can be defined as a process which increases the retractile force and reduces the amount of permanent deformation remaining after removal of the deforming force. Thus vulcanization increases elasticity while it decreases plasticity. It is generally accomplished by the formation of a crosslinked molecular network (Fig. 1.).

FIGURE 1 Network formation.

Effect of Vulcanization on Rubber Molecules

(1) raw rubber, and (2) vulcanized (cross-linked) rubber: (a) soft rubber and (b) hard rubber



Characterization of Vulcanization Process

- Important characteristics
  - the time elapsed before crosslinking starts,
  - the rate of crosslink formation once it starts,
  - the extent of crosslinking at the end of the process.

Characterization of Vulcanization Process

- There must be sufficient delay or scorch resistance (resistance to premature vulcanization) to permit mixing, shaping, forming, and flowing in the mold before vulcanization.
- Then the formation of crosslinks should be rapid and the extent of crosslinking must be controlled.

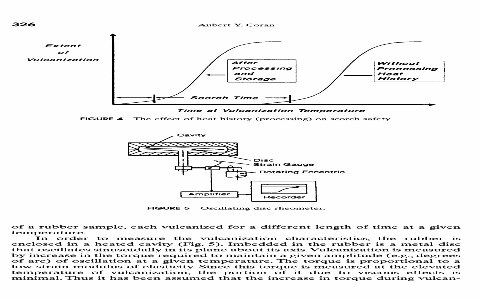


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FIGURE 4 The effect of heat history (processing) on scorch safety.

FIGURE 5 Oscillating disc rheometer.

of a rubber sample, each vulcanized for a different length of time at a given temperature.

In order to measure the vulcanization characteristics, the rubber is enclosed in a heated cavity (Fig. 5). Imbedded in the rubber is a metal disc that oscillates sinusoidally in its plane about its axis. Vulcanization is measured by increase in the torque required to maintain a given amplitude (e.g., degrees of arc) of oscillation at a given temperature. The torque is proportional to a low strain modulus of elasticity. Since this torque is measured at the elevated temperature of vulcanization, the portion of it due to viscous effects is minimal. Thus it has been assumed that the increase in torque during vulcan-

Activators

- In most sulphur-cured rubbers, zinc oxide and stearic acid are added to help initiate the cure.
- In other rubbers, different materials are added which assist the cure in an indirect way.

Curatives

- Curative materials may vary according to the type of elastomer.
- For sulphur-cured rubbers sulphur donors are used for single sulphur cross-links.
- Peroxide cures give good thermal stability due to the short length of the cross-links between polymer chains.
- Fluorocarbons, can have their own specialised cure systems.

Plasticisers/process aids

- Plasticisers need to be compatible with the polymer.
- They reduce hardness and can help with filler dispersion.
- Special types of plasticiser can improve the low temperature flexibility of some rubber types (eg, nitrile and neoprene).

Flame retardants

- Most elastomers support combustion, and the resulting by-products can be extremely hazardous.
- To improve their flame resistance a number of products may be added to the compound, either inorganic or organic.
- They include antimony trioxide, zinc borate, aluminium hydroxide and chlorinated parafins.

Retarders

- Retarders are used to prevent premature curing, or scorching, of compounds during processing and storing.
- During mixing and further processing, the heat can result in premature curing, or pre-curing.
- To prevent this, retarders are mixed with the compound.

Desiccants

- it is necessary to add a desiccant to remove traces of water introduced in fillers or produced from chemical reactions during vulcanization.
- Water can result in uncontrolled porosity in the product.
- The usual agent used for this purpose is calcium oxide (quicklime).

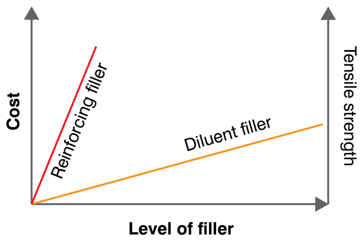
Pigments

- Although most rubber compounds are black, due to the widespread use of carbon black as a filler, coloured rubber compounds are frequently required to add appeal to consumer items.

Example formulation for a 90 IRHD nitrile compound for fuel resistance

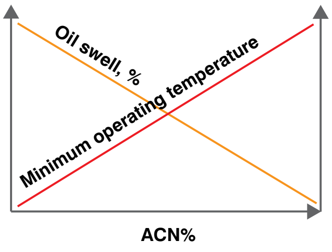
Nitrile rubber 41% ACN	100	High ACN content for fuel resistance
Zinc oxide	5	Cure activator
Stearic acid	1	Cure activator
SRF carbon black	120	Semi-reinforcing filler to obtain hardness
Adipate plasticiser	6	To aid processing
Sulphur	2	Curative
Accelerator	1	To control cure rate
Anti-oxidant	1	To reduce the effects of ageing

Varying quantities and the selection of ingredients can heavily influence the end properties of the compound



The effect of varying the acrylonitrile (ACN) content in a nitrile elastomer:

- Increasing the concentration of ACN can be seen to improve oil resistance, while decreasing its concentration improves low temperature flexibility.



Other Fillers and Additives in Rubber

- Other polymers, such as styrene, PVC, and phenolics.
- Recycled rubber added in some rubber products, but usually 10% or less.
- Antioxidants; fatigue- and ozone-protective chemicals; softening oils; blowing agents in the production of foamed rubber; mold release compounds

Filament Reinforcement in Rubber

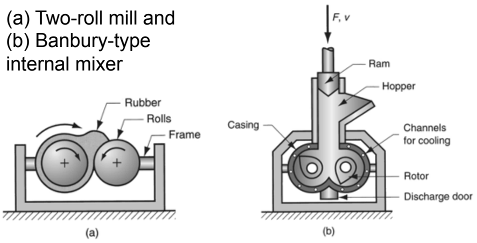
- Many products require filament reinforcement to reduce extensibility but retain the other desirable properties
- Examples: tires, conveyor belts
- Filaments include cellulose, nylon, and polyester
- Fiber-glass and steel are also used (e.g., steel-belted radial tires)
- Continuous fiber materials must be added during shaping; they are not mixed like the other additives

Mixing

- The additives must be thoroughly mixed with the base rubber to achieve uniform dispersion of ingredients
- Uncured rubbers have high viscosity so mechanical working of the rubber can increase its temperature up to 150°C.
- If vulcanizing agents were present from the start of mixing, premature vulcanization would result - the “rubber processor's nightmare”

Mixers in Rubber Processing

- (a) Two-roll mill and (b) Banbury-type internal mixer



Two-Stage Mixing

To avoid premature vulcanization, a two-stage mixing process is usually employed:

- Stage 1 - carbon black and other non-vulcanizing additives are combined with the raw rubber. (rhe master batch)

- Stage 2 - after stage 1 mixing is completed, and cooling time has been allowed, stage 2 mixing is carried out in which vulcanizing agents are added

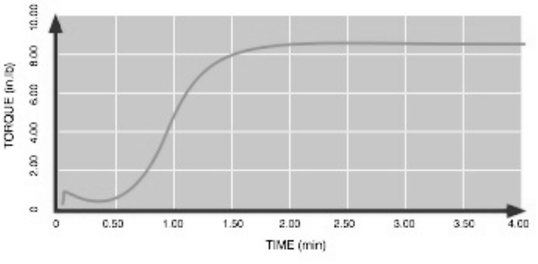
Cure characteristics

- How an elastomer cures over time is measured on a rheometer.

- As the compound cures between the hot platens it becomes stiffer.

- This is measured via a strain gauge connected to an oscillating rotor in contact with the elastomer

Cure characteristics



Shaping and Related Processes for Rubber Products

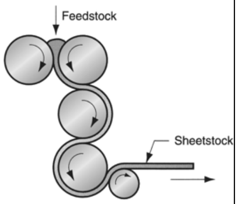
- Four basic categories of shaping processes:
  1. Extrusion
  2. Calendering
  3. Coating
  4. Molding and casting
- Some products require several basic processes plus assembly work (e.g., tires)

Extrusion

- Screw extruders are generally used
- The L/D ratio of the extruder barrel is less than for thermoplastics
  - Typical range 10 to 15
  - Reduces risk of premature cross-linking
- Die swell occurs in rubber extrudates
  - The highly plastic polymer exhibits "memory"
- The rubber has not yet been vulcanized

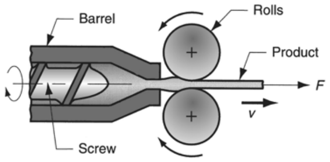
Calendering

- Rubber stock is passed through a series of gaps of decreasing size by a stand of rotating rolls
- Rubber sheet thickness is slightly greater than final roll gap due to die swell



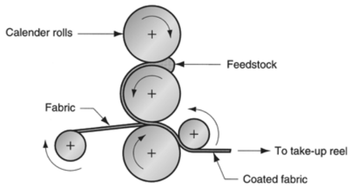
Roller Die Process

Combination of extrusion and calendering that results in better quality product than either extrusion or calendering alone



Coating or Impregnating Fabrics with Rubber

- Important industrial process for producing tires, conveyor belts, inflatable rafts, and waterproof cloth



Molded Rubber Products

- Molded rubber products include shoe soles and heals, gaskets and seals, suction cups, and bottle stops
- Also, many foamed rubber parts are produced by molding
- In addition, molding is an important process in tire production

Molding Processes for Rubber

- Principal molding processes for rubber are
  1. Compression molding
  2. Transfer molding
  3. Injection molding
- Compression molding is the most important because of its use in tire manufacture

Molding Processes for Rubber

- Curing (vulcanizing) is accomplished in the mold in all three molding processes
- This represents a departure from previous shaping methods
- Other shaping methods use a separate vulcanizing step

Vulcanization Chemicals and Times

- When first invented by Goodyear in 1839, vulcanization used sulfur (about 8 parts by weight of S mixed with 100 parts of NR) at 140°C for about 5 hours
  - Vulcanization with sulfur alone is no longer used, due to long curing times
- Various other chemicals (e.g., zinc oxide, stearic acid) are combined with smaller doses of sulfur to accelerate and strengthen the treatment
  - Resulting cure time is 15-20 minutes

Tires and Other Rubber Products

- Tires are about 75% of total rubber tonnage
- Other important products:
  - Footwear
  - Seals
  - Shock-absorbing parts
  - Conveyor belts
  - Hose
  - Foamed rubber products
  - Sports equipment

Tires and Other Rubber Products

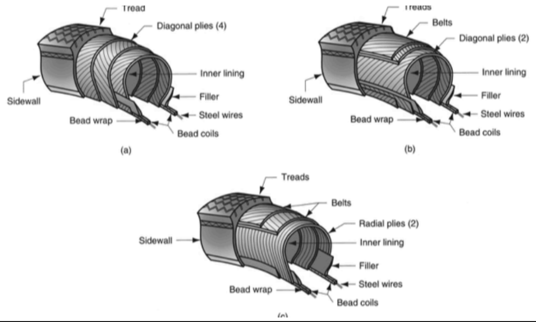
Pneumatic Tires

- Functions of pneumatic tires on vehicle :
  - Support the weight of the vehicle, passengers, and cargo
  - Transmit the motor torque to propel the vehicle
  - Absorb road vibrations and shock to provide a comfortable ride
- Tires are used on automobiles, trucks, buses, farm tractors, earth moving equipment, military vehicles, bicycles, motorcycles, and aircraft

Tire Construction

- A tire is an assembly of many components
  - About 50 for a passenger car tire
  - Large earthmover tire has as many as 175
- The internal structure of the tire, known as the *carcass*, consists of multiple layers of rubber-coated cords, called *plies*
  - The cords are strands of nylon, polyester, fiber glass, or steel, which provide inextensibility to reinforce the rubber in the carcass

Three Tire constructions: (a) diagonal ply, (b) belted bias, and (c) radial ply



Tire Production Sequence

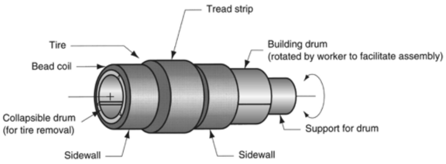
- Tire production is summarized in three steps:
  1. Preforming of components
  2. Building the carcass and adding rubber strips to form the sidewalls and treads
  3. Molding and curing the components into one integral piece
- Variations exist in processing depending on construction, tire size, and type of vehicle

Preforming of Components

- Carcass consists of multiple components, most of which are rubber or reinforced rubber
- These components and others are produced by continuous processes
  - They are then pre-cut to size and shape for subsequent assembly
  - Other components include: bead coil, plies, inner lining, belts, tread, and sidewall

Building the Carcass

- Prior to molding and curing, the carcass is assembled on a *building drum*, whose main element is a cylindrical arbor that rotates



Other Rubber Products: Rubber Belts

- Widely used in conveyors and pulley systems
- Rubber is ideal for these products due to its flexibility, but the belt must have little or no extensibility
  - Accordingly, it is reinforced with fibers, commonly polyester or nylon
- Fabrics of these polymers are usually coated by calendering, assembled together to obtain required number of plies and thickness, and subsequently vulcanized by continuous or batch heating processes

Other Rubber Products: Hose

Two basic types:

1. Plain hose (no reinforcement) is extruded tubing
2. Reinforced tube, which consists of:
   - Inner tube - extruded of a rubber compounded for particular liquid that will flow through it
   - Reinforcement layer - applied to inner tube as fabric, or by spiraling, knitting, braiding
   - Outer layer – compounded for environment and applied by extrusion

Other Rubber Products: Footwear

- Rubber components in footwear: soles, heels, rubber overshoes, and certain upper parts
- Molded parts are produced by injection molding, compression molding, and certain special molding techniques developed by the shoe industry
- The rubbers include both solid and foamed
- For low volume production, manual methods are sometimes used to cut rubber from flat stock

Processing of Thermoplastic Elastomers

- A thermoplastic elastomer (TPE) is a thermoplastic polymer that possesses the properties of a rubber
- TPEs are processed like thermoplastics, but their applications are those of an elastomer
- Most common shaping processes are injection molding and extrusion
  - Generally more economical and faster than the traditional processes for rubbers that must be vulcanized

TPE Products

- Molded products: shoe soles, athletic footwear, and automotive components such as fender extensions and corner panels
- Extruded items: insulation coating for electrical wire, tubing for medical applications, conveyor belts, sheet and film stock
- No tires of TPE