RUBBER – ITS IMPLICATIONS TO ENVIRONMENTAL HEALTH

(HYDROCARBON RUBBERS)

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WHAT IS “RUBBER”?

- A range of different types
  - commodity or specialised
  - both natural and synthetic
- Easily recognised - soft and compliant
  - compared with ceramics, metals or plastics
- Strong (usually) and very tough
  - resistant to fracture, tear, abrasion, etc.
- Capable of large-strain elasticity
  - recoverable extensions of several hundred percent possible
- Properties a result of unique molecular structure

DIFFERENT RUBBERS

- **Commodity (hydrocarbon)**
  - natural rubber (NR)
  - styrene-butadiene rubber (SBR)
  - ethylene-propylene rubbers (EPM, EPDM)
  - butadiene rubber (BR)
- **High/low permeability rubbers**
  - silicone rubber MQ, VMQ, PVMQ, FVMQ, etc) – high permeability
  - butyl (IIR), halobutyl rubbers (CIIR, BIIR) – low permeability
- **Oil-resistant rubbers**
  - nitrile (NBR), hydrogenated nitrile (HNBR) rubbers
  - acrylic rubber (ACM)
- **Fire-resistant rubbers**
  - chloroprene (“neoprene”) rubber (CR)
  - epichlorohydrin rubber (ECO)
- **High temperature rubbers**
  - fluorocarbon rubbers (FKM, FFKM)
- **Liquid castable rubbers**
  - polyurethane (EU)
  - polysulphide (T)

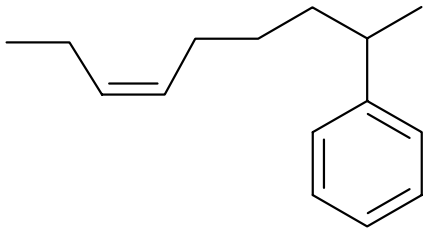
SUBTLE CHANGES IN MOLECULE CAN PROVIDE EITHER PLASTIC OR RUBBER

- Polyethylene, $-(CH_2-CH_2)_n-$
  - very flexible molecule,
  - but regular structure introduces crystallinity
  - polyethylene is a plastic
  - softer than many plastics
  - used in packaging, etc

- Polypropylene, $-(CH_2-CHMe)_n-$
  - stiffer than polyethylene
  - regular structure – hence crystalline
  - polypropylene is a plastic
  - good combination of stiffness, strength (and price)
  - widespread applications

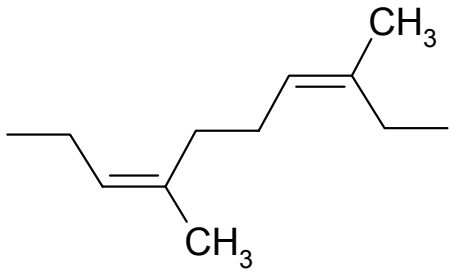
- Ethylene-Propylene Copolymers
  - Irregular structure disrupts crystallinity
  - 50:50 E:P to 75:25 E:P (by wt) are rubbers
  - the basis of EPDM rubber
  - used in hose, car door & boot seals, etc.

OTHER HYDROCARBON RUBBERS



styrene-butadiene rubber

SBR



natural rubber

NR

- NR polymer (a polyterpene) is obtained from the latex of the Hevea Brasiliensis tree
- SBR polymer is product of the oil industry
- Average MW can be around 500k for NR, around 100k for SBR
- These are the principal tyre rubber polymers

But why is rubber elastic?
Why the exceptional large-strain elasticity?

ELASTICITY

- Elasticity is the ability to recover from a deformation
  - when applied stress is removed, an elastic material will recover completely its original shape
- Many materials show elasticity up to a limit – beyond this additional stress causes irreversible 'plastic' flow
  - elastic limit may be measured in terms of applied strain ($\Delta l/l$)
  - for metals and ceramics, elastic limit may be <0.001% strain
  - for plastics, limit may lie at percentage values
  - for rubber limit may be at strains of several hundred of percent

But ultimate elastic performance only with **vulcanised rubbers**

Vulcanisation is post-polymerisation chemical treatment
Prior to vulcanisation, rubber is visco-elastic

EFFECT OF VULCANISATION

- Physical - vulcanisation suppresses viscous behaviour and enhances elastic behaviour
  - removes tack and reduces temperature sensitivity
  - remarkable elasticity develops
- Chemical – vulcanisation links molecules together ('crosslinking')

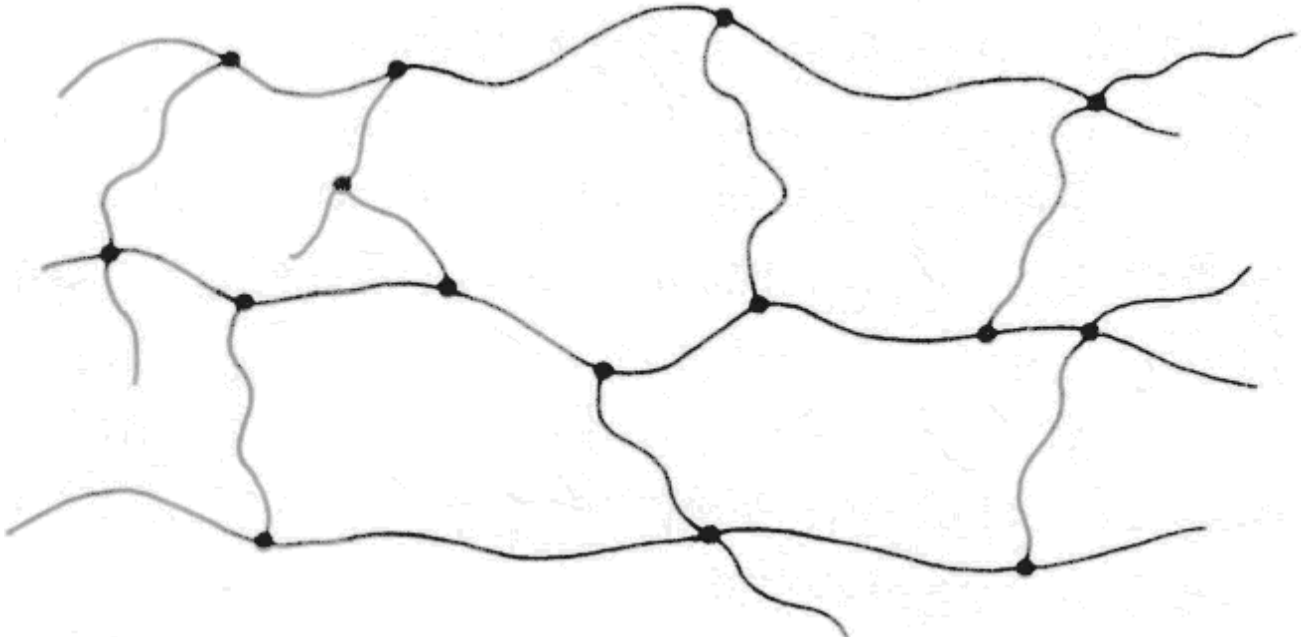
  e.g. with sulphur (simplistically)

  $$RH + S_x + RH \rightarrow R{-}S_y{-}R + H_2S$$
- Linking all the molecules together creates a single molecule of infinite molecular weight

POLYMERS OF INFINITE MW

Cannot flow, cannot be melted or dissolved

Will recover elastically from imposed strains



SULPHUR VULCANISATION USED IN TYRE RUBBERS

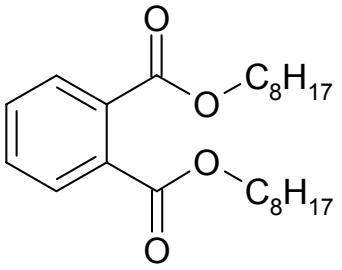
- Well established
  - for fine tuning product properties
  - for good control in processing

- Chemistry relies on a cocktail of chemicals:
  - vulcanising agent (sulphur)
  - accelerators and activators
  - inhibitors or retarders (stop premature reaction)
  - antioxidants (protect against heat)
  - antiozonants (protection in service)

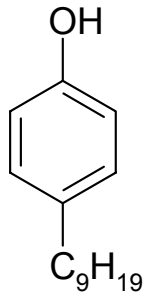
- Other ingredients include:
  - fillers (carbon black) for reinforcement
  - softeners (process oils)

INGREDIENT MIX WELL ESTABLISHED - IT DOES NOT INCLUDE

- Phthalate plasticisers
  - used in PVC and nitrile rubbers
  - don't function in hydrocarbon rubbers



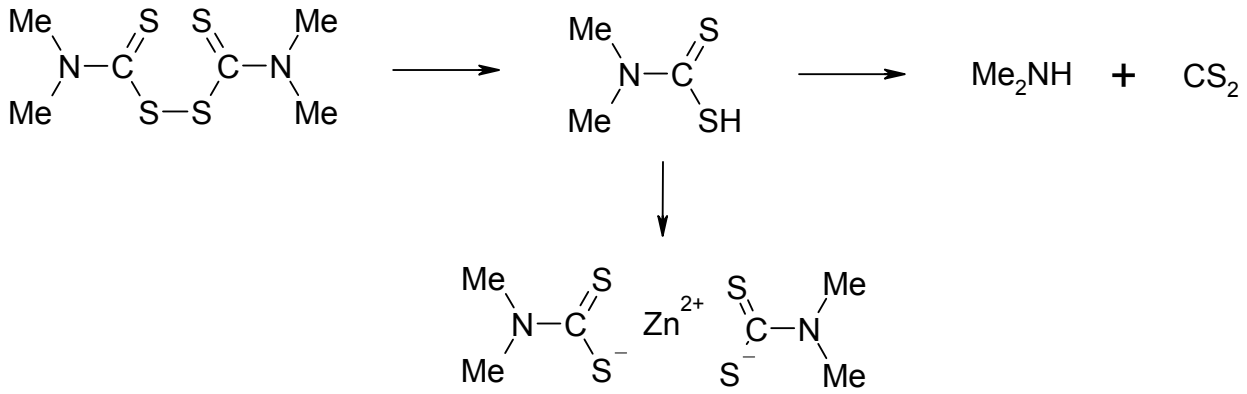
- Monoalkylphenols
  - used to make non-ionic surfactants
  - surfactants not used in tyres



- Cadmium
  - Zinc oxide is 99% pure

BUT VULCANISATION DOES CREATE NEW PRODUCTS

e.g. thiuram accelerators generate: amines, CS_2 and zinc dithiocarbamates



Other accelerators give different amines – e.g. CBS → cyclohexylamine

Amines give ketones by side-chain oxidation – e.g. 6PPD → MIBK

cyclohexylamine → cyclohexanone

LOW MW SPECIES IN VULCANISED RUBBER

Include

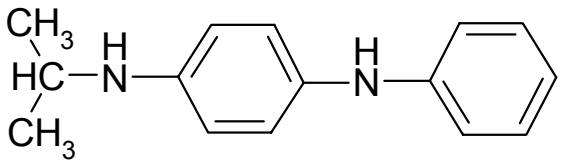
- orginal ingredients of mix
- by-products of vulcanisation

All encapsulated in a molecular network

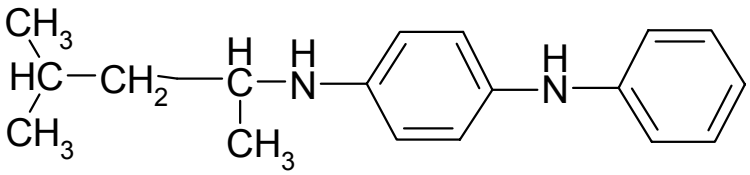
- which may hold some species in
  - i.e. organics well-solvated by network
- and squeeze other species out
  - i.e. those that try to crystallise out from solvation

Elastic properties of network force crystallisable species to the surface – vulcanised rubbers "bloom"

COMPONENTS OF BLOOM CAN INCLUDE….



IPPD



6PPD

Aromatic amine antiozanants

- N-isopropyl-N‘-phenyl-*p*-phenylenediamine (IPPD)
- N-1,3-dimethylbutyl-N‘-phenyl-*p*-phenylenediamine (6PPD)

Tyre rubber has a basic surface

Zinc salts

- Zinc dimethyldithocarbamate $(Me_2NCS_2)_2Zn$

Water leaches zinc from tyre rubber

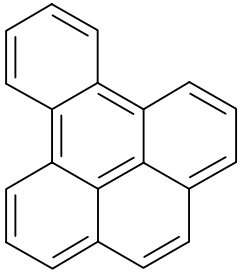
SURFACE CHARACTER OF RUBBER

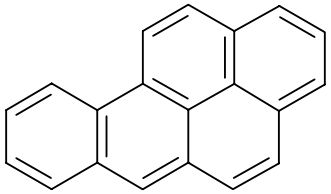
Contact dermatitis linked with skin contact with rubber

- Causative agents include the components of bloom
- Effect depends on individual sensitivity and extent of contact
- Not normally associated with transient contact
  - e.g. not associated with handgrips, matting, dinghies, etc.
- Usually seen in somebody wearing rubber
  - e.g. goggles, elasticated clothing, etc

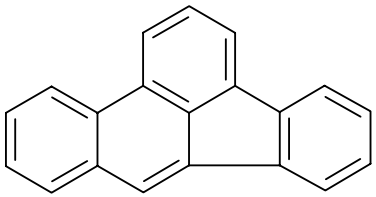
- Contact dermatitis not expected with rubber granulate

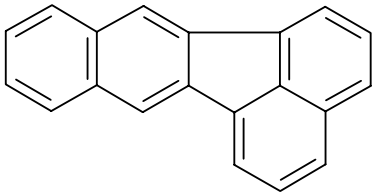
Nilsson et al. (2005) looked at extraction by (synthetic) sweat
– found health risks insignificant

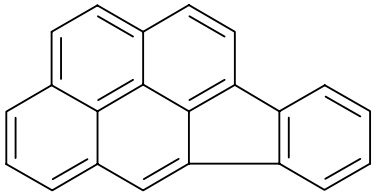


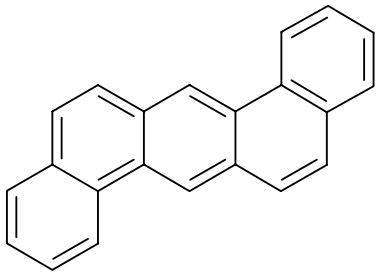


Polycyclic aromatic hydrocarbons









POLYCYCLIC AROMATIC HYDROCARBONS

- Lubricating oils are (solvent) extracted to remove aromatics
- These extracts – 'aromatic process oils' – are excellent plasticisers/softeners for tyre rubbers
- Improve processing and product performance (wet grip etc.)

- But they are rich in PAHs
- PAH content in the range 20-30%
- And they do contain the carcinogenic (e.g. five-ring) types
- Aromatic process oils carry labelling

T	Toxic
R45	May cause cancer

Occupational health issues will see replacement of these oils

PAHs ARE IN TYRE RUBBER – DO THEY COME OUT?

1973-75 BRMA survey of airborne benzo[*a*]pyrene in ten UK tyre factories found:

- concentrations from zero to 28 ng/m^3
- no correlation with process or factory area
- strong correlation with seasons and weather

Nutt (1984) repeated this with simultaneous measurements of inside (tyre factory) and outside air

- found no excess of B[*a*]P in factory air

Willoughby (1994) analysed PAHs from laboratory vulcanisations at up to 200ºC

- found only two-to-four ring PAHs in volatiles

PAHs ARE IN TYRE RUBBER – CAN THEY LEACH OUT?

Norwegian Institute for Water Research (2005) carried leachate tests on granulate:

- found only two-to-four-ring PAHs in leachate

Log K_{ow} values

- ca. 3-4 for three-ring
- ca. 4-5 for four-ring
- ca. 6 for five-ring

- So five-ring PAH is ca. 10^6 time more likely to partition in an organic phase rather than in water
- Five-ring PAHs will stay in the vulcanised rubber

PAHs ARE ALREADY IN THE ENVIRONMENT

- **PAHs are in the air from combustion processes**
  - transport, power generation, cigarettes, etc.
- **Routinely monitored in ambient air**
  - Annual avs. for benzo[*b*]fluoranthe and benzo[*a*]pyrene ca. 1 ng/m^3 in Manchester UK
- **Carried on soot particles and washed out of air by rain**
- **Pass into rivers and lakes – and then into sediments**

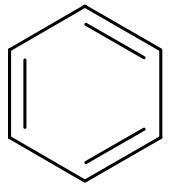
Nilsson et al (2005) studied PAHs in sand in a children's playground with used tyre components

- Found distribution of PAHs did not reflect that in tyre rubber
- Concluded that the PAHs arose from deposition from the air

Additional risks from PAHs in tyre granulate judged insignificant

BENZENE

- Present in original vulcanisate from polymer/carbon black interaction
  - polymer displaces adsorbed benzene from black surface
- May also be taken up by tyre rubber in service
  - benzene and rubber will have a strong affinity
  - affinity will work against elastic forces
  - so benzene will ‘push’ its way in



- Benzene has been found in air above tyre granulate

Dye et al. (2003) monitored several species in air of indoor sports halls. The smallest margin against WHO guidance values was for benzene.

Benzene max. found, 2.3 µg/m^3 WHO/EC limit, 5.0 µg/m^3

Is there a cause for concern?

BENZENE IS ALREADY IN THE ENVIRONMENT

- Unleaded gasoline contains benzene
- Up to 50% of premium gasoline can be aromatic
- Benzene is ubiquitous in urban air

Air in urban flat (Frankfurt am Main)[a]	10.2 µg/m^3 (mean)
Air in filling station (breathing zone)[b]	27 µg/m^3 (max)
Air inside vehicle (driving)[b]	120 µg/m^3 (max)

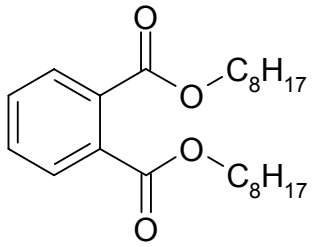
a) Heudorf & Hentschel (1995)

b) WHO (2000)

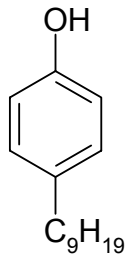
- All the above are in excess of WHO guidelines
- Sports hall air is actually below the guidance value
- Norwegian Inst of Pub Health (2006) – concluded that the levels found do not pose a cancer risk

PHTHALATES AND ALKYLPHENOLS

- Not ingredients of tyre rubber
- But various researchers have found them in leachates from tyre granulate
- Environmental concerns (endocrine disruptors)



- These must be picked up from the environment in service
  - i.e. tyres are an environmental fate for phthalates and alkylphenols



- A reminder that scrap tyre granulate will be a variable product

- Standards/testing important

ZINC

- ZnO is an activator in sulphur vulcanisation
- Forms zinc salts as a by-product of vulcanisation chemistry
- Zinc salts can bloom in vulcanisates
- Expect zinc in leachates from any sulphur vulcanisate
  - and it is found
- But care is needed to avoid spurious data from background contamination (e.g. from galvanising)

ZINC LEACHING

Lab trials - effect of pH (Liu et al., 1998)

pH 3.5	pH 5.0	pH 7.0
23.5 mg/l	17.5 mg/l	3.38 mg/l

Field trials (Humphrey and Katz, 2001)
Levels (mg/l) in trench with granulate (background in parenthesis)

	Peat	Clay	Glacial Till
Unfiltered	2.39 (0.04)	0.75 (0.18)	0.57 (0.13)
Filtered	0.065 (0.009)	0.12 (0.007)	0.076 (0.004)

Away from trench, Zn levels rapidly decay to background levels

ZINC LEACHING

Overall conclusions are:

- Tire sheds placed above or below the water table have a negligible impact on water quality
- There may be a localised environmental impact

Zinc testing should figure in quality standards

RISKS FROM RUBBER GRANULATE IN SPORTS SURFACES

- A number of species are present in rubber granulate
  - from the ingredients used
  - from reactions of vulcanisation
  - from exposure in previous use (tyres)

- Many are held in tightly within the rubber
- Some are expelled to the surface (bloom)
- There is no demonstrable health risk
- There may be a localised environmental impact

SUSTAINABILITY

SBR & EPDM polymers are products of oil industry

NR polymer is sustainable - but vulcanisate requires synthetic chemicals

A different way?

SUSTAINABILITY

400k tons per year of scrap tyres generated in the UK alone

Unsightly, unhealthy, a fire risk – and a wasted resource

If it's a suitable feedstock for sports surface granules – use it