

UNIVERSITY OF ZAGREB
FACULTY OF CHEMICAL ENGINEERING AND TECHNOLOGY

Polymer science and technology

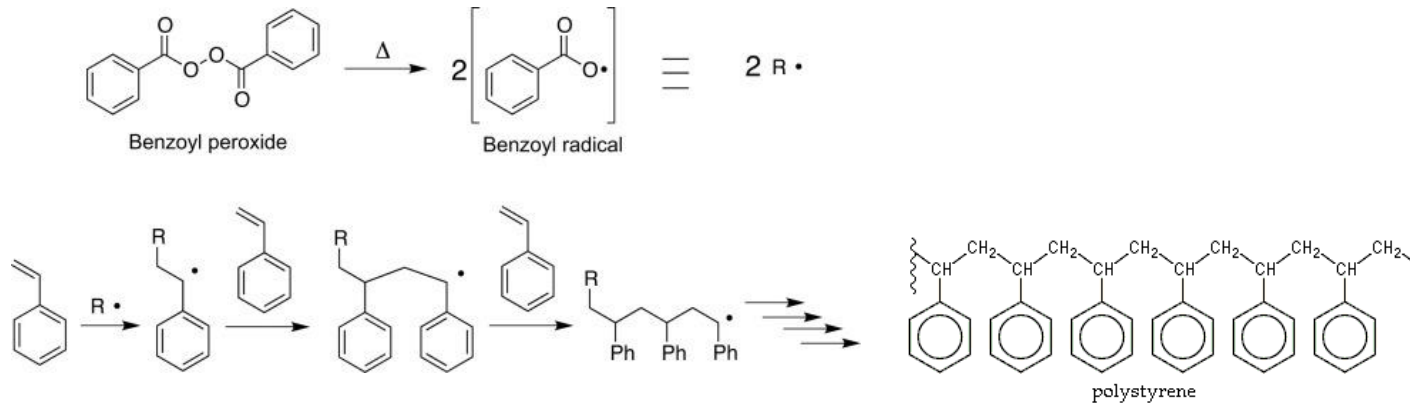
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Polystyrene (PS)

- **Thermoplastic** aromatic polymer, known since 1839
- Eduard Simon, an apothecary from Berlin **distilled** an **oily substance** from storax, the resin of the Oriental sweetgum tree, he named **styrol** (it was styrene monomer)
- Several days later **styrol hardened into styrol oxide**, because he presumed an oxidation
- It was shown that the same transformation takes place in the absence of oxygen
- 80 years later it was realized that **heating of styrol** starts a chain reaction that **produces macromolecules**
- Substance received its present name, **polystyrene**
- In **1931** being **produced commercially** by I.G. Farben
- In **1949** **polystyrene foam** named “**Styropor**” was produced

Polystyrene (PS)

- Free radical polymerization with free radical initiators (benzoyl peroxide, redox systems and azo compounds)
- Bulk, suspension and solution polymerization of styrene



- ❑ Reaction is exothermic, the monomer–polymer mixture must be cooled
- ❑ Bulk or mass polymerization, the reaction is controlled by using a two-stage polymerization process. In the first stage, the styrene is polymerized in a stirred tank reactor at 80 °C where a low conversion is achieved (prepolymerizer)
- ❑ The mixture of dispersed polymer in monomer is then transferred to a tubular reactor and pure molten PS emerges from the reactor is pumped through through an extruder to produce the desired finished granulate (2–5 mm pellets)

Polystyrene (PS)

- The polystyrene produced by **mass polymerization** is a **fully transparent** (amorphous), atactic, low cost thermoplastic known as **general purpose polystyrene (GPPS)** or **crystal-clear polystyrene**



- In the case of **solution polymerization**, styrene is dissolved in a **suitable solvent** such as ethylbenzene, which makes **temperature control** much easier
- **Presence of solvent** reduces the **molecular weight** and lowers the transparency due to a higher degree of impurities
- **Suspension process** is also very common, especially in the production of expanded polystyrene (EPS) and high-impact polystyrene (HIPS)

Polystyrene (PS)

- The **commercially important form of PS is atactic**, phenyl groups are randomly distributed on both sides of the polymer chain
- Large phenyl groups prevents the chains from aligning to achieve crystallinity
- **High optical clarity, low price, very brittle, low impact strength, poor barrier to oxygen and water vapour**
- **Soluble in benzene, chloroform, tetrahydrofurane, carbon disulfide, chlorinated aliphatic hydrocarbons,**
- **Syndiotactic PS (sPS)** is produced (in small quantities) with **metallocene catalysts, highly crystalline**, excellent chemical resistance, low dielectric constant, high heat distortion temperature
- Used in electrical and electronic materials, as well as in temperature-resistant automotive and appliance applications

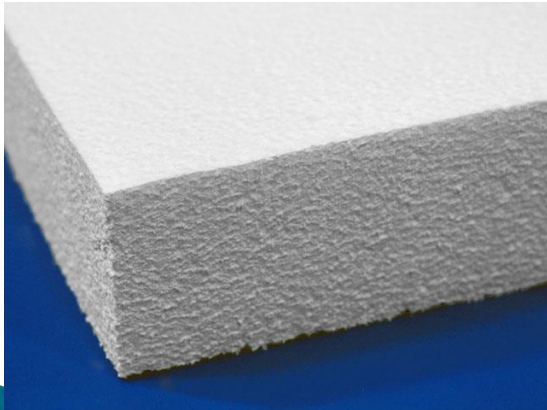
Polystyrene (PS)

- PS can be **solid** or **foamed**
- **Solid PS** is used in the **food-service industry** as rigid trays and containers (yogurt and water cups), **disposable eating utensils**, plates, and bowls, CD cases, smoke detector housings and many other objects where a rigid, economical plastic is desired
- ❑ **Medicine** – labware such as petri dishes and tissue culture trays
- ❑ **Resistant to radiation sterilization** due to high aromatic content
- ❑ Special PS synthesized by anionic polymerization with narrow molecular weight distribution, $PDI < 1.1$, used as calibration standard for GPC
- ❑ GPC standard PS 1 g = 180 \$; GPPS 1 kg = 1–2 \$



Polystyrene (PS)

- **Foamed PS** – Expanded polystyrene (EPS)
- ❑ PS foams are **good thermal insulators** – often used as **building insulation material**, good damping properties – **widely used in packaging**
- ❑ The beads of **PS expanded in mould** many times their original size using **steam and pentane** until they completely fill the space
- ❑ If the mould is in the shape of the final product, the part is removed from the machine and the process is complete. More commonly, **EPS is moulded into a large rectangular block** and then cut into the final shape using hot wires



Polystyrene (PS)

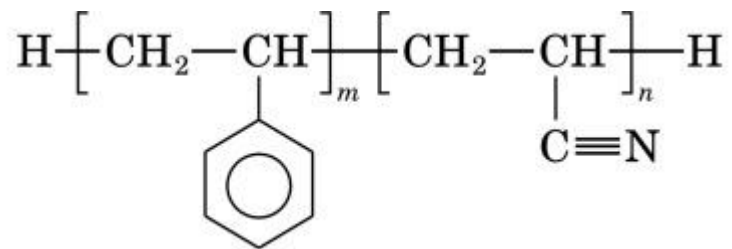
- EPS is a **rigid and tough**, closed-cell foam with a density 10–30 kg/m³
- Lightweight material, **problem for collecting and recycling**
- **EPS is easily flammable**; flame retardants need to be added
- According to Croatian regulation for buildings 22+ m EPS can not be used for facades



Polystyrene modification

➤ Styrene-acrylonitrile copolymer (SAN)

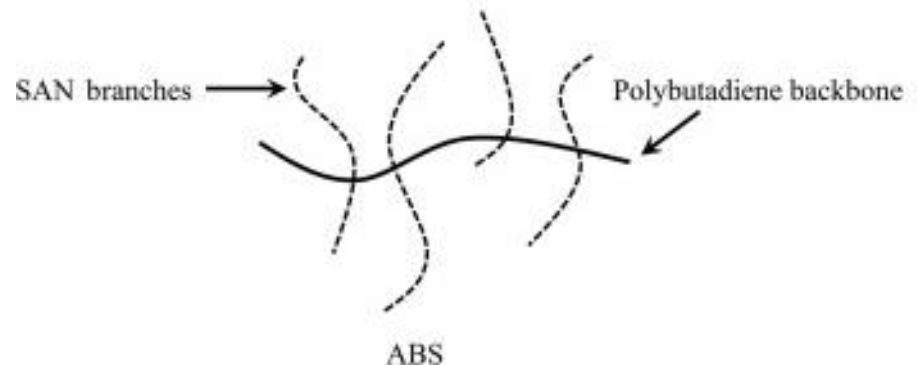
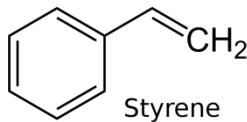
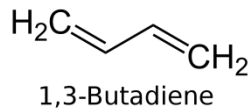
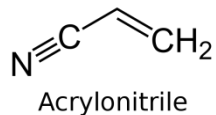
- ❑ 20–30% acrylonitrile (AN) content
- ❑ Because of the polar nature of the AN, it has **increased resistance to solvents**
- ❑ **Improved tensile strength, impact strength, thermal resistance**
- ❑ Higher AN content adds a yellow tint
- ❑ Application for dials, knobs, and covers for domestic appliances, electrical and car equipment, for picnicware and housewares



Polystyrene modification

➤ Acrylonitrile–butadiene–styrene copolymer (ABS)

- ❑ 15–35% AN, 5–30% butadiene, 40–60% styrene
- ❑ SAN is formed in a polymerization system in the presence of polybutadiene rubber; final product is a complex mixture consisting of SAN copolymer, a graft polymer of SAN and polybutadiene and some free polybutadiene rubber
- ❑ Partly grafted SAN to polybutadiene (PBD) backbone, partly two–phase system of SAN and PBD
- ❑ Combines properties of SAN with greatly improved impact resistance



Polystyrene modification

➤ Acrylonitrile–butadiene–styrene copolymer (ABS)

- ❑ AN contributes to chemical resistance, fatigue resistance, hardness, and rigidity
- ❑ Styrene gives shiny surface and hardness, rigidity
- ❑ PBD provides toughness and ductility at low temperatures
- ❑ By changing the proportions of its components, ABS can be prepared in different grades
- ❑ **Houseware** (refrigerator doors, luggage, furniture frames), **housing and construction** (pipes, conduits, bathtubs), **transportation** (automotive instrument panels, light housings)
- ❑ Common material in 3D printing



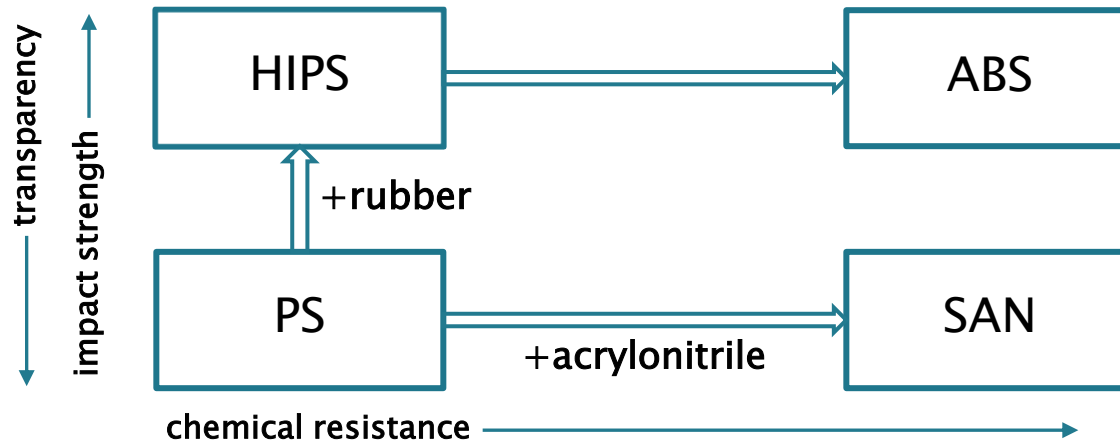
Lego®



Samsonite

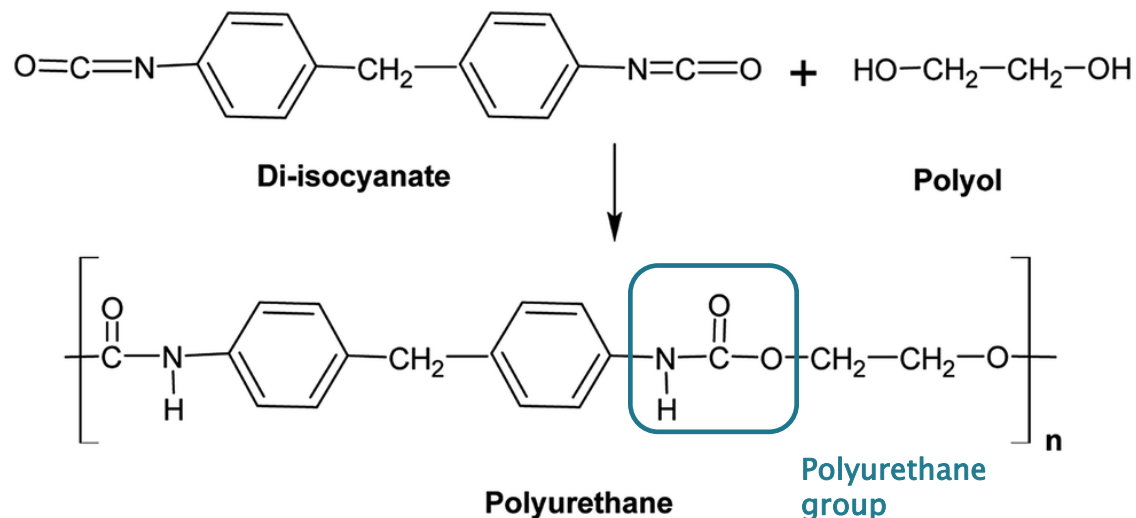
Polystyrene modification

- **High-impact polystyrene (HIPS)/impact-resistance PS (PS-I)**
 - ❑ Continuous polystyrene matrix and dispersed rubber phase, produced by polymerization of styrene in the presence of polybutadiene dissolved in styrene
 - ❑ Polymerization takes place simultaneously in two ways: **Graft copolymerization** where the growing polystyrene chain reacts with a double bond of the polybutadiene. As a result, **several PS chains are attached to one polybutadiene molecule**; **homopolymerization of polystyrene without the reaction with the present polybutadiene**
 - ❑ Cheaper than ABS, similar application
 - ❑ ABS and HIPS are white, not transparent as GPPS and SAN



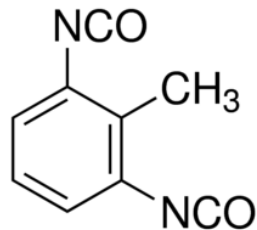
Polyurethanes (PU/PUR)

- Polyurethanes (PURs) are a special group of polymeric materials that are in many ways different from most of the other plastic types
- Polyurethanes are **produced from a wide range of starting materials** (monomers) and is therefore a **class of polymers, not a distinct compound**
- Formed by reacting a **polyol** (an alcohol with **two or more reactive hydroxyl groups, OH**) with a **diisocyanate** (two NCO functional groups)
- First time synthesized in 1937 at IG Farben

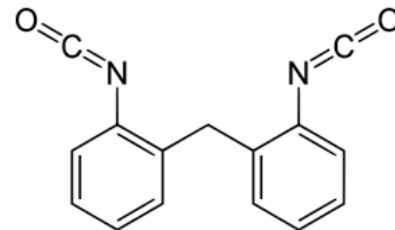


Polyurethanes (PU/PUR)

- **Polyfunctional alcohols or dialcohol monomers are:**
 - ❑ ethylene glycol $(\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH})$
 - ❑ diethylene glycol $(\text{HO}-\text{CH}_2-\text{CH}_2\text{O}-\text{CH}_2-\text{CH}_2-\text{OH})$
 - ❑ 1,4-butanediol $(\text{HO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH})$
 - ❑ 1,6-hexanediol $(\text{HO}-[\text{CH}_2]_6-\text{OH})$
- Most commonly used **polyfunctional isocyanates** are:
 - ❑ toluene diisocyanate (TDI)
 - ❑ methylene-diphenyl diisocyanate (MDI)
- These aromatic isocyanates are cheaper and more reactive than aliphatic isocyanates



TDI



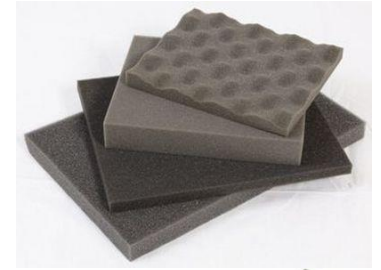
MDI

Polyurethanes (PU/PUR)

- Reaction of diisocyanates with polyols takes place in the **presence of a catalyst** (commonly tertiary amines), or upon **exposure to UV light**
- Molecules can be **linear or crosslinked**, most PUs are crosslinked and therefore thermosetting polymers
- Most **common application of PU is as solid foams**, which requires the presence of a gas, or **blowing agent**, during the polymerization step
- Achieved by adding H_2O , which reacts with isocyanates to form CO_2
- **Type of foam** can be controlled by **regulating the amount of blowing agent** and by the addition of surfactants which change the rheology of the polymerising mixture
- Foams can be either "**closed-cell**", most of the original bubbles or cells remain intact, or "**open-cell**", where the bubbles have broken
- **Open-cell foams feel soft** and allow air to flow through, they are comfortable when used in seat cushions or mattresses. **Closed-cell foams** are used as **rigid thermal insulation**

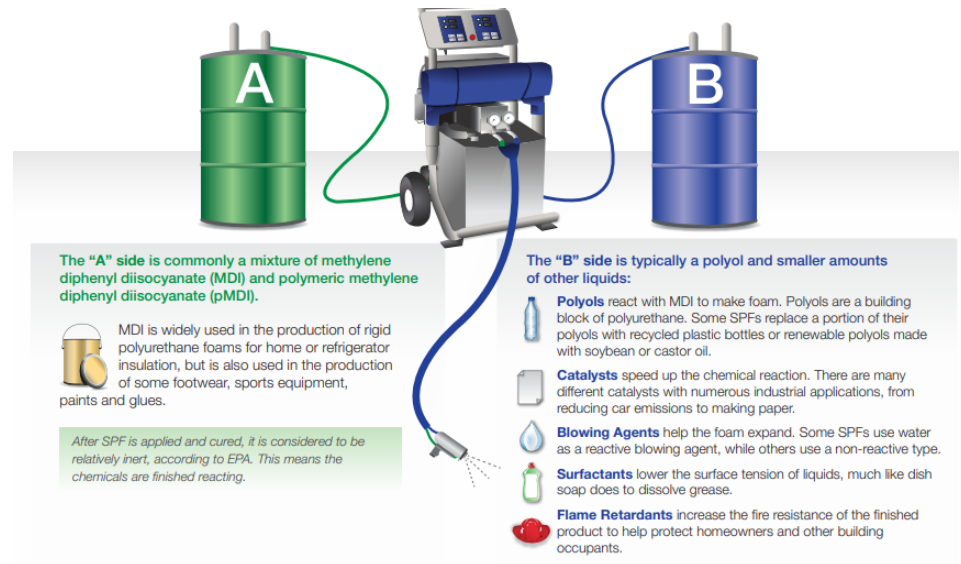
Polyurethanes (PU/PUR)

- **Flexible**, high-resilience foamed products (**open cell**)
 - ❑ **mattresses**
 - ❑ **upholstered furniture**
 - ❑ **carpet underlays**
 - ❑ car parts like cushions, backs, and armrests
- **Rigid** foamed products (**closed cell**)
 - ❑ **insulations** for commercial and residential buildings
 - ❑ **insulations** for tanks, pipes, water heaters, refrigerators and freezers



Polyurethanes (PU/PUR)

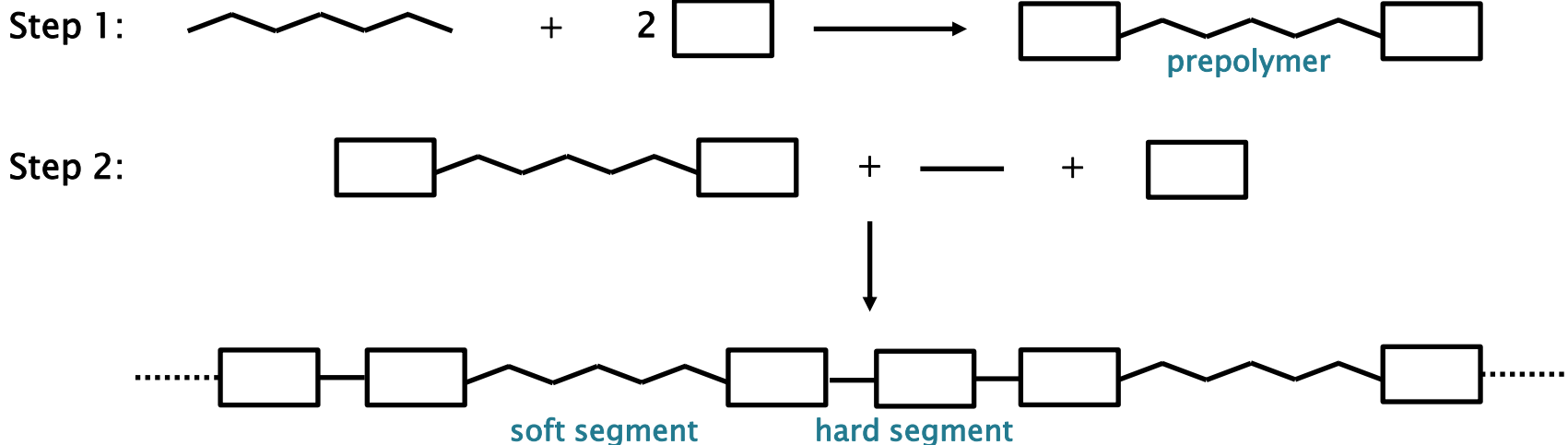
Spray foam insulation



Polyurethanes (PU/PUR)

Thermoplastic polyurethane (TPU)

- Block copolymer consisting of alternating sequences of hard and soft segments or domains formed by:
 - ❑ diisocyanates + short-chain diols (so-called chain extenders) → **hard segments**
 - ❑ diisocyanates + long-chain diols → **soft segments**
- By varying the ratio, structure and/or molecular weight of the reaction compounds, variety of different TPU can be produced

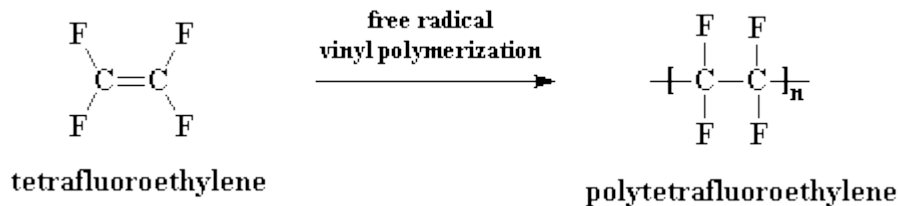


Polyurethanes (PU/PUR)

- The polarity of the **hard segments** creates a strong interaction between them, causing a high degree of aggregation and order, **forming crystalline areas** in a soft and flexible matrix
- The **crystalline areas act as physical cross-links**, which account for the **high elasticity level of TPU**
- **TPU is thermoplastic elastomer**, similar as metallocene PP (2nd lecture)
- These "**pseudo crosslinks**", **when heated disappear**, classical extrusion and injection molding, can be used for processing
- **Applications** include automotive instrument panels, sporting goods, medical devices, footwear, inflatable rafts, outer cases of mobile electronic devices
- Wire and cable jacketing, hose and tube
- Thermoplastic elastomer **used in 3D printing**

Poly(tetra fluoroethylene) (PTFE)

- The commonly known **brand name of PTFE is Teflon**, discovered in 1938 by DuPont
- PTFE is produced by free-radical polymerization of tetrafluoroethylene



- **Tetrafluoroethylene can explosively decompose to tetrafluoromethane and carbon so special apparatus is required for the polymerization to prevent hot spots** that might initiate this side reaction
- PTFE is poorly soluble in almost all solvents; the **polymerization is conducted as an emulsion in water** which gives a suspension of polymer particles

Poly(tetra fluoroethylene) (PTFE)

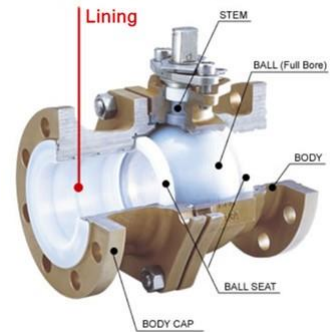
- **Properties**
- Rigid, white, hydrophobic, **self-lubricating polymer**
- **Non-reactive**, because of the strength of carbon-fluorine bonds (one of the strongest single bonds in chemistry)
- **Third lowest coefficients of friction of any solid**
- PTFE is so slippery that insects cannot get a grip and tend to fall off, only known surface to which a gecko cannot stick



Poly(tetra fluoroethylene) (PTFE)

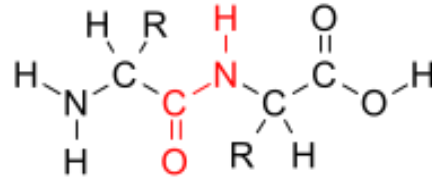
➤ Application

- Major application (50% of PTFE production) – **insulation of wiring in aerospace and computer applications** (e.g. coaxial cables) since it has excellent dielectric properties. **High-performance substitute for the PE** commonly used in low-cost applications
- **Bearings, gears, slide plates and applications with sliding action of parts** (self-lubricating)
- Linings for chemical process equipment (chemical inertness)
- Aerosol lubricant sprays
- **Non-stick coatings for frying pans and cookware**
- **Breathable water resistant fabric (Gore-Tex)**



Polyamides

- Polyamides are crystalline polymers typically produced by the **condensation of a diacid and a diamine**, repeating units linked by **amide bonds**



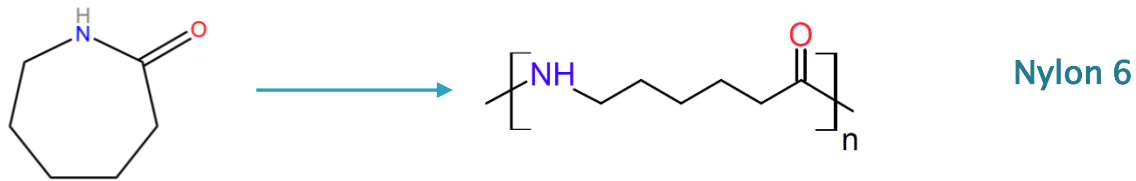
- Amine group and a carboxylic acid group can be on the same monomer, or the polymer can be constituted of two different bifunctional monomers, one with two amine groups, the other with two carboxylic acid groups
- **Naturally occurring polyamides are proteins** (1 st lecture)
- Synthetic polyamides are classified as **aliphatic** or **aromatic** (Aramids)
 - ❑ **Aliphatic** – Nylon PA 6, PA 66, PA 11, PA 12, PA 46,...
 - ❑ **Aromatic** – Kevlar and Nomex

Polyamides

Aliphatic polyamides (Nylon)

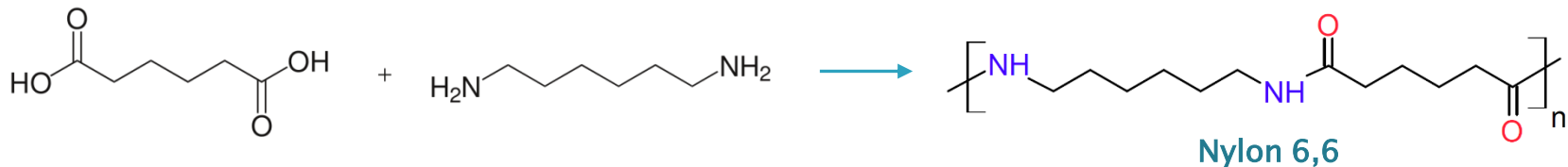
➤ Nylon 6 (polycaprolactam)

- ❑ Nylon 6 is not a condensation polymer, but instead is **formed by ring-opening polymerization of caprolactam** (already contains amide bond)



➤ Nylon 6,6 (Nylon 6/6)

- ❑ Synthesized by polycondensation of **hexamethylenediamine** and **adipic acid** (each having 6 C atoms)

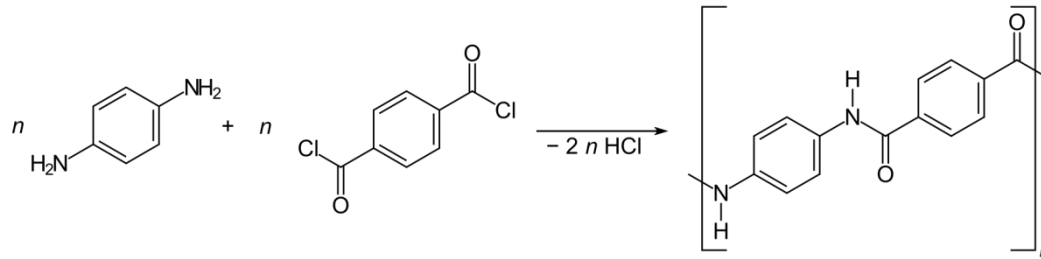


- ❑ Nylon 6,6 – direction of the amide bond reverses at each bond
- ❑ Nylon 6 – amide bonds lie in the same direction

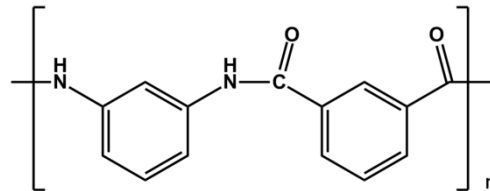
Polyamides

Aromatic (Aramid) polyamides

- Aramid is a shortened form of aromatic polyamide
- Kevlar
 - ❑ *para*-aramid, monomers *p*-phenylene-diamine and terephthaloyl chloride



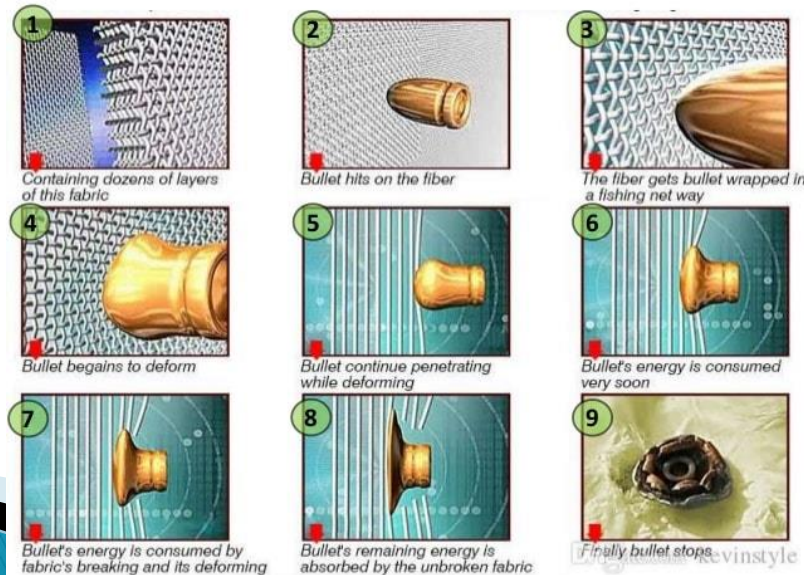
- Nomex
 - ❑ *meta*-aramid, monomers *m*-phenylene-diamine and isophthaloyl chloride



Polyamides

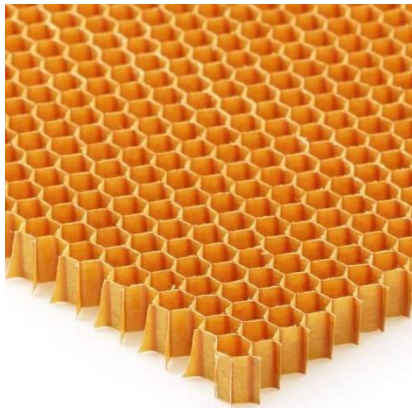
➤ Properties and application

- ❑ Nylon fibres are tough, possessing **high tensile strength and elasticity**, highly resistant to abrasion and chemicals
- ❑ Used when high mechanical strength, rigidity, good stability under heat and/or chemical resistance are required
- ❑ **Fibers for textiles and carpets**
- ❑ **Aramid fibers** are heat-resistant and strong fibers
- ❑ Used in **aerospace and military applications**, for ballistic-rated body armor fabric (bulletproof vests, similar to UHMWPE)
- ❑ **Kevlar** has five times larger than steel tensile strength-to-weight ratio



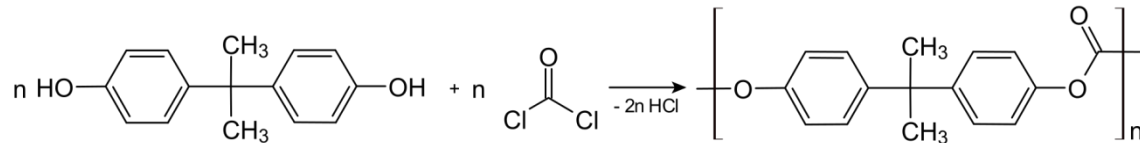
Polyamides

- **Nomex** honeycomb structures and Mylar–Nomex laminates, are used extensively in **aircraft construction**
- Stiff, thin **Nomex** sheet structures are used to make strong and lightweight, **honeycomb sandwich composite** found in aircraft parts such flooring panels, interior walls, storage bins, exterior control surfaces, engine nacelles and helicopter blades
- Firefighting, military aviation, and vehicle racing industries use Nomex to create **clothing and equipment that can withstand intense heat**
- Racing car drivers wear **driving suits and gloves constructed of Nomex** and other fire retardant materials



Polycarbonates (PC)

- Thermoplastic polymers containing carbonate groups, **carbonyl group flanked by two alkoxy groups** ($-\text{O}-(\text{C}=\text{O})-\text{O}-$)
- Main polycarbonate material is produced by the reaction of **bisphenol A (BPA)** and **phosgene COCl_2**

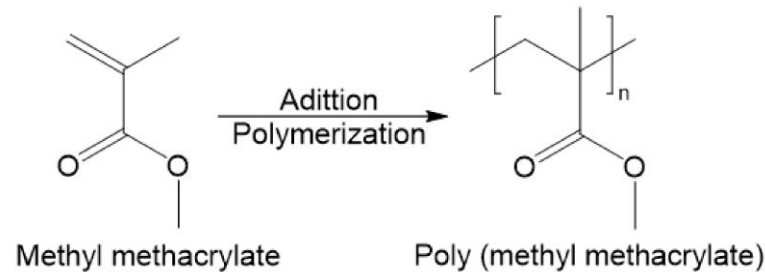


- High impact-resistance, highly transparent to visible light
- **Application**
 - ❑ Construction industry, **roofing sheets and sound walls**
 - ❑ Compact discs, DVDs, and Blu-ray discs
 - ❑ Automotive, aircraft industry, **headlamp lenses, bullet-resistant „glass”, racing helmets visors**
 - ❑ **Drinking bottles, sunglass/eyeglass lenses, swimming and safety goggles**



Poly(methyl methacrylate) (PMMA)

- Transparent and rigid thermoplastic material known as **acrylic** or **acrylic glass** or **plexiglass**



- It has almost **perfect transmission of visible light**, it retains these properties over years of exposure to ultraviolet radiation (PC is prone to UV degradation) and weather, ideal substitute for glass
- PMMA is an **economical alternative to polycarbonate (PC)** when tensile strength, flexural strength, **transparency**, and **UV tolerance** are more **important than impact strength**, chemical resistance, and heat resistance

Poly(methyl methacrylate) (PMMA)

➤ Application

- ❑ Car rear lamps, plane windows, internally lighted signs for advertising and directions, domed skylights, swimming pool enclosures, aircraft canopies, instrument panels, luminous ceilings, eye lenses (hard contact and implants)

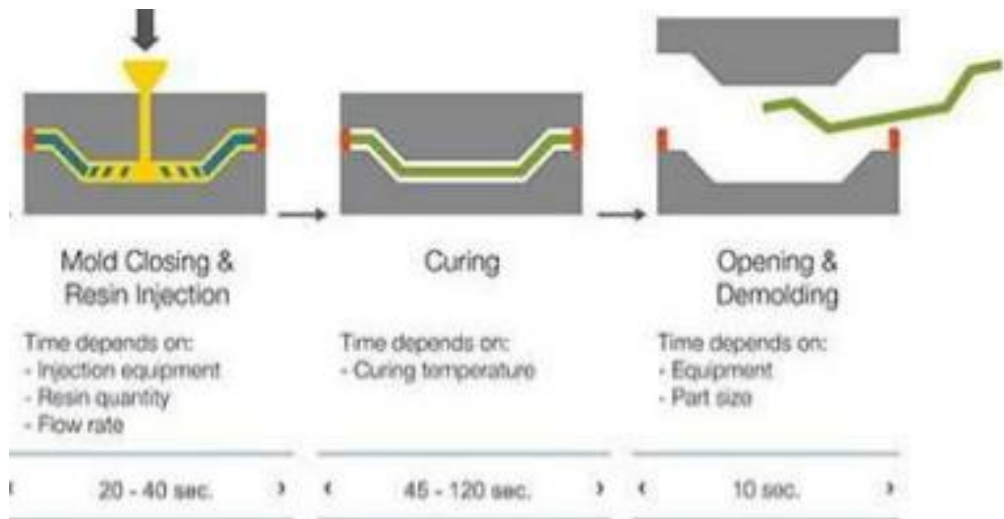


THERMOSET POLYMERS

- Obtained by **condensation** polymerization, **crosslinked (cured)**
- **Soft solid or viscous liquid** prepolymer (**resin**) before crosslinking
- Curing is induced by **heat, radiation** or mixing with a **curing agent** (catalyst, hardener)
- Heat is often generated by the reaction of the resin with a curing agent
- When heated, the **resin solidifies into the specified shape**, formation of **crosslinks**
- Process is **irreversible** because chains are chemically bonded – **crosslinked, forming network, 3D-structure**
- Thermoset polymers can not be soften on heating, **can not be melted**
- **During the heating** they are subjected to **degradation** because primary chemical bonds are destroyed
- **Can not be reshaped**, it is a problem during the recycling

THERMOSET POLYMERS

- During polymerization simultaneously manufactured (shaped in mould)
- General properties:
 - ❑ more brittle in nature
 - ❑ regular structure results in hard and strong material
- Main application: coatings, adhesives, electrical insulation



Thermoplastics vs thermosets

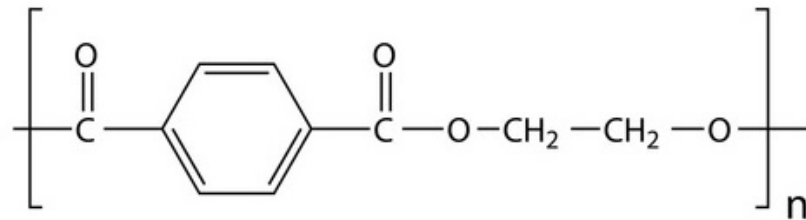
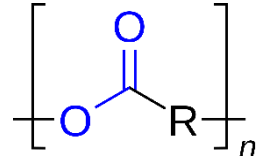
Feature/Property	Thermoplastics	Thermosets
Molecular structure	Linear/branched polymer: weak molecular bonds in a straight-chain formation	Network polymers: high level of crosslinking with strong chemical molecular bonds
Melting point	Melting point lower than the degradation temperature	Melting point higher than the degradation temperature
Mechanical	Flexible and elastic. High resistance to impact (10x more than thermosets)	Inelastic and brittle. Strong and rigid
Polymerisation	Addition polymerisation: polymerised before processing	Polycondensation polymerisation: polymerised during processing
Size	Size is expressed by molecular weight	Size is expressed by crosslink density
Recyclability	Recyclable and reusable by the application of heat	Non-recyclable
Chemical resistance	Highly chemical resistant	Heat and chemical resistant
Process thermal aspect	Melting thermoplastics is endothermic	Crosslinking thermosets is exothermic
Service temperature	Lower continuous use temperature (CUT) than thermosets	Higher CUT than thermoplastics
Solubility	Can dissolve in organic solvents	Do not dissolve in organic solvents

General properties and applications of thermosetting plastics (**resins**)

- Polyester resins
- Alkyd resins
- Epoxy resin
- Amino resin
- Silicone resins

Polyester resins

- Polymers that contain the ester functional group in main chain
- Can be thermoplastic or thermoset



- PET is thermoplastic (saturated) polyester!
- Polyester resins constitute 75% of resins used
- Unsaturated polyesters (resins) are condensation polymers formed by the reaction of polyols (organic compounds with multiple alcohol or hydroxy functional groups), with unsaturated (or in some cases saturated) dibasic acids
- Polyols are glycols including ethylene glycol, propylene glycol, and diethylene glycol; typical acids used are phthalic acid, isophthalic acid, terephthalic acid, and maleic anhydride

Polyester resins

- Unsaturated polyesters are sold to manufacturers as a **solution of resin in reactive diluent, styrene is the most common diluent**
- The diluent allows control over the viscosity of the resin, and is also a participant in the curing reaction
- The initially liquid resin is converted to a solid by **cross-linking chains by creating free radicals at unsaturated bonds**, which propagate to other unsaturated bonds in adjacent molecules, linking them in the process
- The initial free radicals are induced by adding **initiator (organic peroxides)** and **catalyst (transition metal salts)**
- Polyester resins cure exothermically (as all other resins), use of excessive initiator and catalyst can cause charring or even ignition during the curing process

Polyester resins

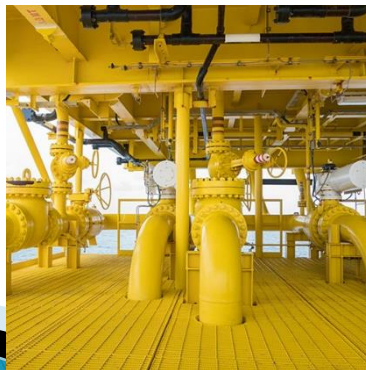
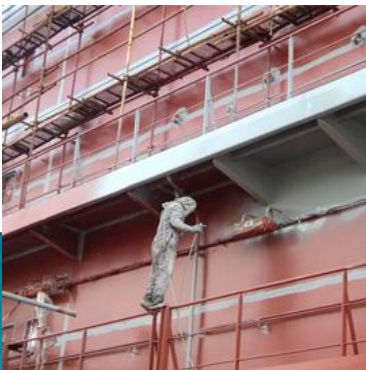
➤ Application

- ❑ Unsaturated polyester can be used in form of pure resin or compounded with fillers
- ❑ **Construction industry** (nonreinforced or glass fiber reinforced products), **automotive industry**, industrial wood and furniture finishing
- ❑ Cast items such as **shirt buttons**, **knife and umbrella handles**, and **encapsulation of electronic assemblies**
- ❑ Polyester compounds have been formulated for the manufacture of **bathroom fixtures**
- ❑ Floor-tiles have been manufactured by mixing them with fillers such as limestone or silica



Alkyd resins

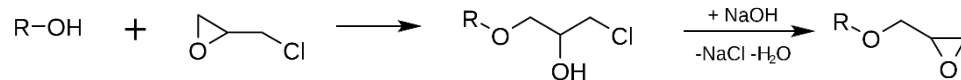
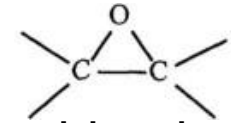
- Polyester resins modified by the addition of fatty acids
- Alkyds are derived from **polyols**, **dibasic acids** or anhydride and **triglyceride oils**
- Alkyd resins may be classified as **drying** and **nondrying**
- **Drying resins** – fatty acids are derived from **unsaturated** plant and vegetable oils (linseed, sunflower oil etc.), **cured by the oxygen in air** (autocatalytic reaction)
- **Nondrying resins** – fatty acids are derived from **saturated** oils (coconut oil), **cured by the temperature and catalyst**
- Used in **synthetic paints, varnishes and enamels**; principal applications are furniture and architectural coatings, product finishes, special-purpose coatings and automotive primers (40% of coatings are alkyd)



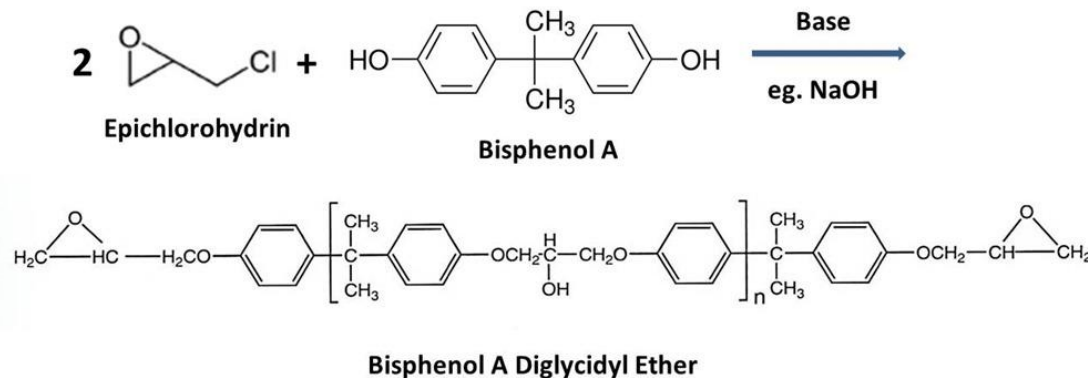
	Corrosion rate (mm year ⁻¹)
Uncoated stainless-steel	0.840
Alkyd coated stainless-steel	0.0021

Epoxy resins

- An epoxide is a cyclic ether with a three-atom ring
- Most of the commercially used epoxy monomers are produced by the reaction of a compound with acidic hydroxy groups and epichlorohydrin

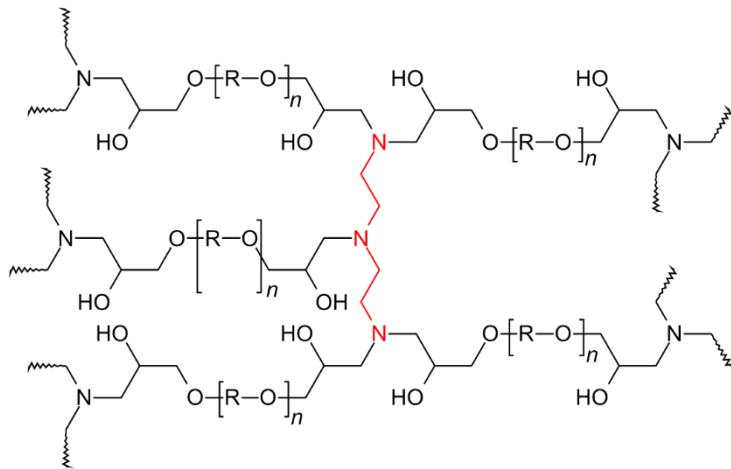


- Hydroxy group may be derived from aliphatic diols, polyols, **phenolic compounds** or dicarboxylic acids
- The most common epoxy resins are based on reacting epichlorohydrin with **bisphenol A**



Epoxy resins

- **Curing of epoxy resins**
- Curing is an **exothermic reaction** and may produce sufficient heat to cause thermal degradation if not controlled
- Curing may be achieved by **reacting an epoxy with itself** (homopolymerisation) or by **forming a copolymer with hardeners**
- Chemicals that can be used to cure epoxy (hardeners): **amines, acids, acid anhydrides, phenols, alcohols, thiols and photosensitive chemicals**



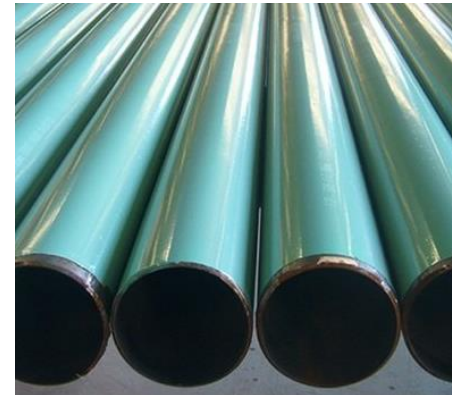
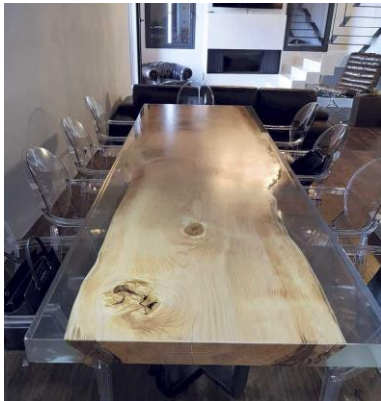
Structure of a cured epoxy glue

triamine hardener – resin

The resin's epoxide groups have reacted with the hardener and are not present anymore

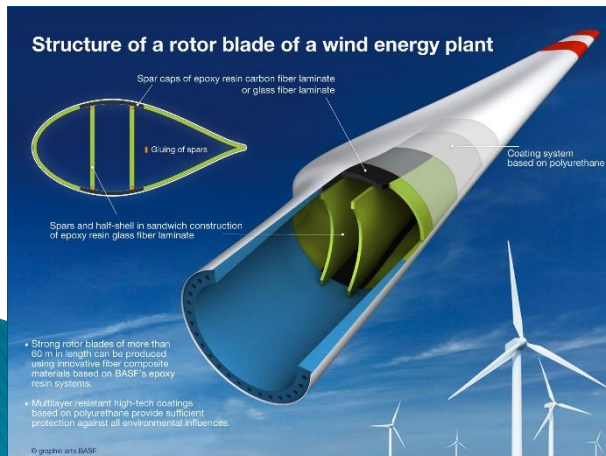
Epoxy resins

- **Application**
- **Paints and coatings** – corrosion protection of steel pipes and fittings used in the oil and gas industry and concrete reinforcing rebar, primers to improve the adhesion of automotive and marine paints, metal cans and containers coating to prevent rusting for acidic foods, industrial and decorative flooring
- **Adhesives** – **high-performance adhesives** used in the construction of aircraft, automobiles, bicycles, boats, skis and other applications where high strength bonds are required



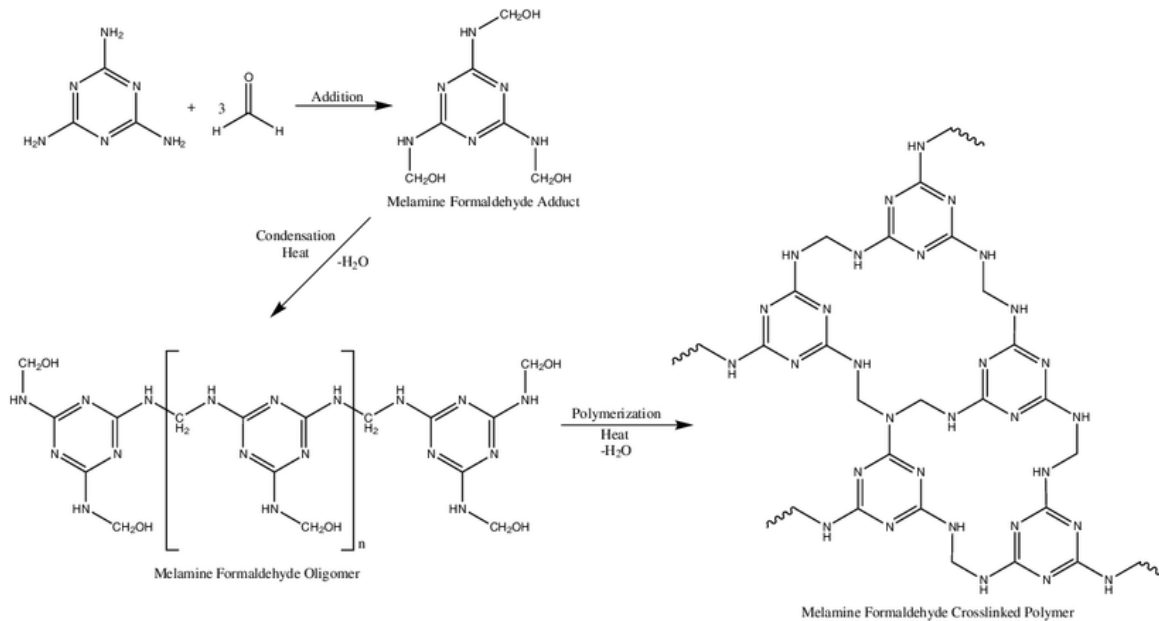
Epoxy resins

- **Application**
- **Composites** – production of **fiber-reinforced composites**, more expensive than polyester resins, but produce stronger and more temperature-resistant composite; used in **aerospace industry** and **wind turbines**. **Prone to UV degradation** so need to be coated with UV-protection (usually polyurethane paint)
- **Electronics industry** – employed in motors, generators, transformers, insulators and semiconductor encapsulants. **Excellent electrical insulators** and protect electrical components from short circuiting, dust and moisture. **Epoxy is primary resin used in overmolding integrated circuits, transistors and making printed circuit boards**

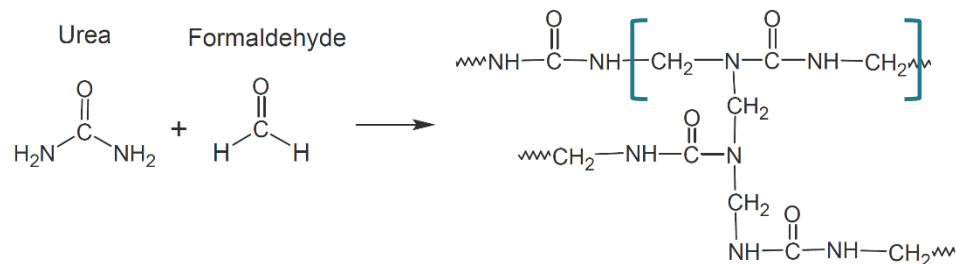


Amino resins

Amino resins (**aminoplasts**) are condensation thermosetting polymers of **formaldehyde** with either **urea** or **melamine**



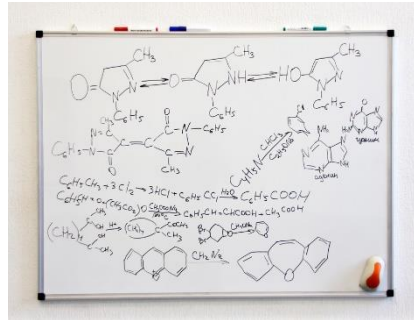
Melamine formaldehyde



Urea formaldehyde

Amino resins

- **Melamine formaldehyde**
- Adhesives for laminate flooring, whiteboards, kitchen cabinets and furniture making (outer layer on particle board)

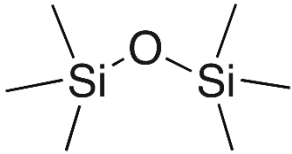


- **Urea formaldehyde**
- Adhesives for particle board, medium-density fibreboard (MDF), molded objects (electronic components), foam insulation



Silicone resins

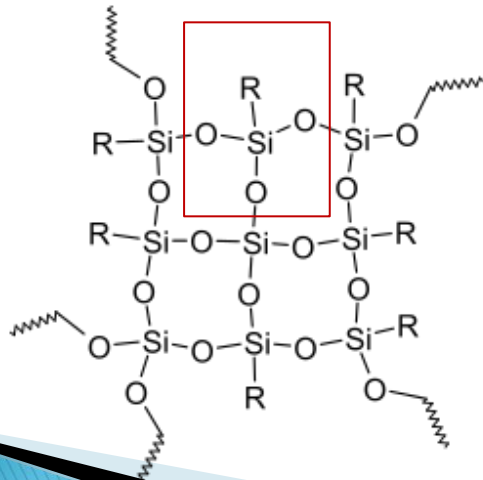
- Si – Silicon [*sīl'ī-kōn*], naturally occurring element
- Silicone [*sīl'ī-kən*], polymer made of siloxane groups (polysiloxane)



- Inorganic polymers or semi-organic, known since 1963
- **Backbone made up entirely of silicon-oxygen bonds with organic substituents attached to each silicon atom**
- By varying the –Si–O– chain lengths, side groups, and crosslinking, silicones can be synthesized with a wide variety of properties and compositions, can vary in consistency from liquid to gel to rubber to hard plastic
- The most common polysiloxane is linear polydimethylsiloxane (PDMS – more in the elastomer lecture), the **second-largest group of silicone materials is based on silicone resins**

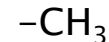
Silicone resins

- highly branched, cage-like oligosiloxanes
- General formula $R_nSiX_mO_y$
- ❑ R is non reactive substituent methyl or phenyl group
- ❑ X is a functional group Hydrogen (H), Hydroxyl group (OH), Chlorine (Cl) or Alkoxy group (OR)
- ❑ These groups are further condensed to give highly crosslinked, insoluble polysiloxane networks
- Use in a broad range of products, pressure-sensitive adhesives, paints and coatings

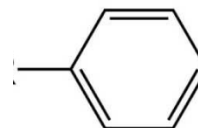


Substituents R:

methyl group

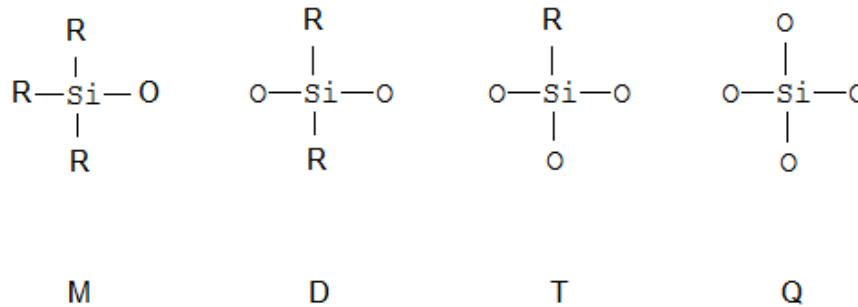


phenyl group



Silicone resins

- Resin structure can be combination of these groups, R is methyl group



- M = Me_3SiO , D = Me_2SiO_2 , T = MeSiO_3 , Q = SiO_4
- Network of only Q groups becomes fused quartz
- Most abundant silicone resins are built of D and T units (DT resins) or from M and Q units (MQ resins), however many other combinations (MDT, MTQ, QDT) are also used in industry
- Resins have very varied structures depending on the quantity of M, D, T, Q groups

Silicone resins

- **Excellent heat stability**, can withstand temperatures of up to 500 °C
- **Excellent water-repellent characteristics**
- **Excellent resistance weathering**, especially by UV-radiation
- Good dielectric properties, even at temperatures of up to 250 °C, use in **high-performance electrical insulation products**, effective protection against weathering and high temperatures
- **Paints industry** is a major user of silicones resins as binders to improve the heat resistance of paints and renderings
- Special silicone resins are used in the **water-repellent treatment of construction materials**, of facades and in the consolidation of ancient monuments

