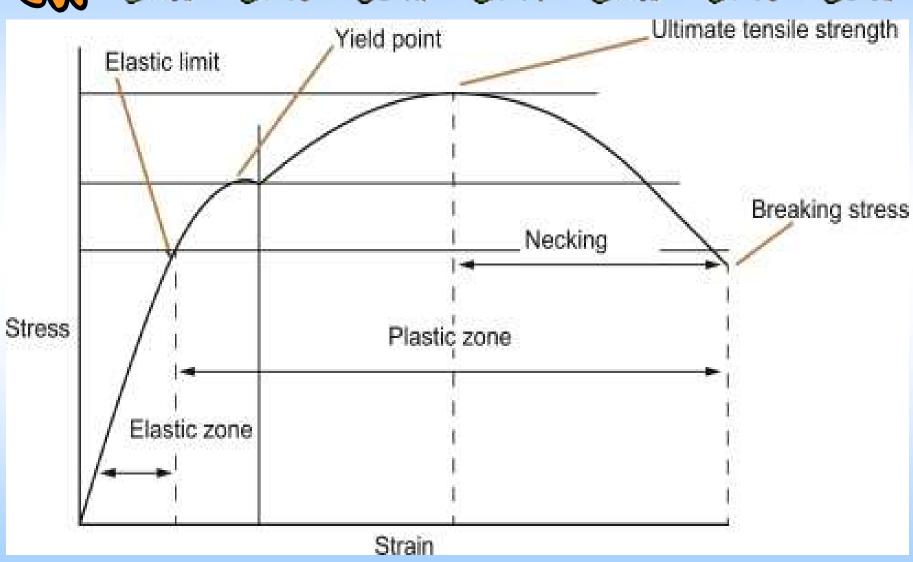
#### **Textile chemistry**



#### 5. Man mede fibres



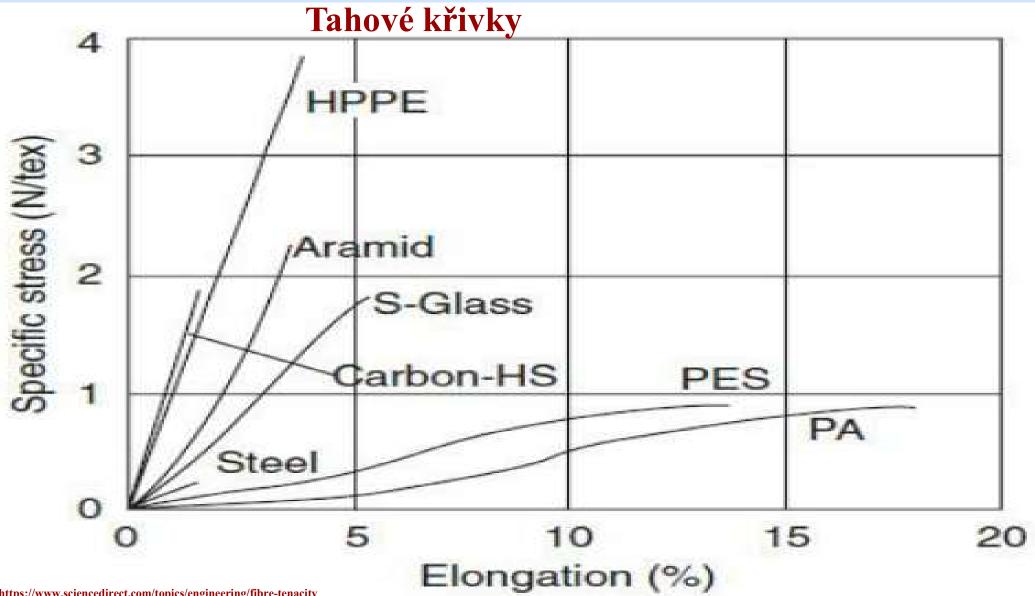
"But she never wears anything but man-made fibres."



Tahová křivka

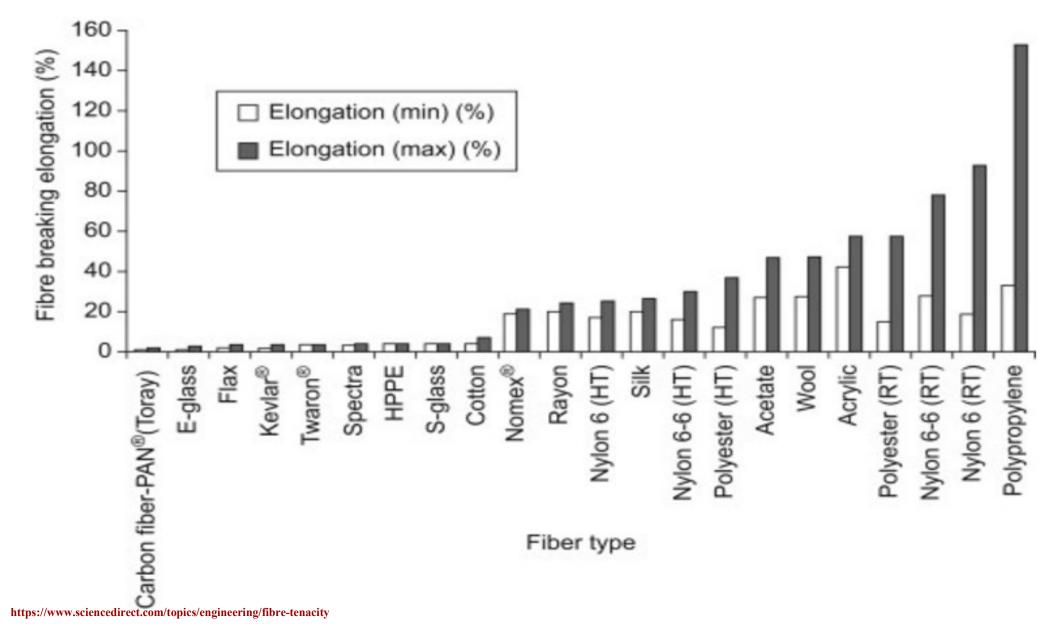






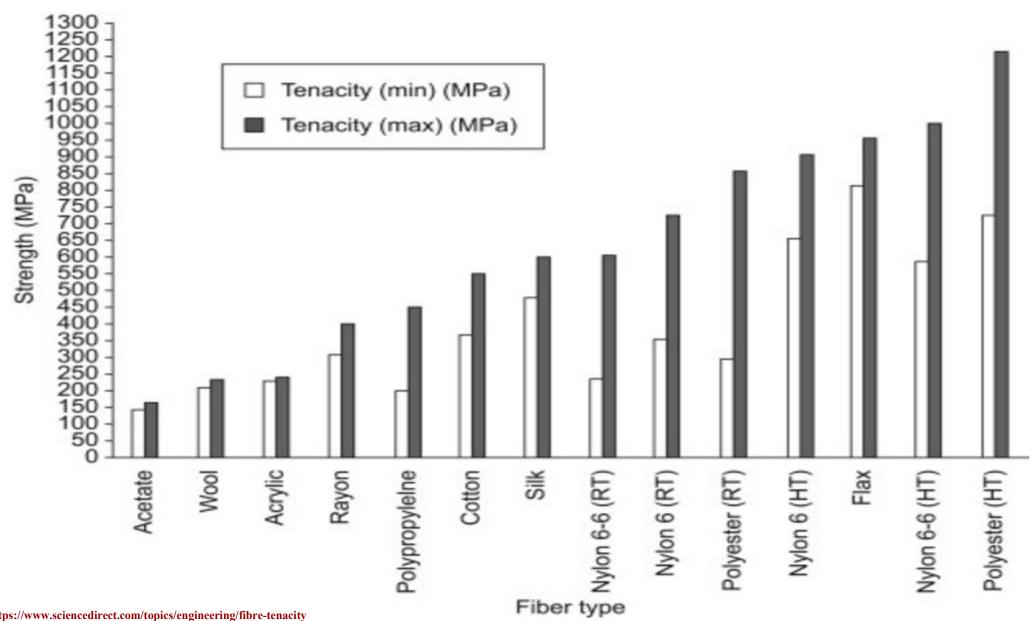






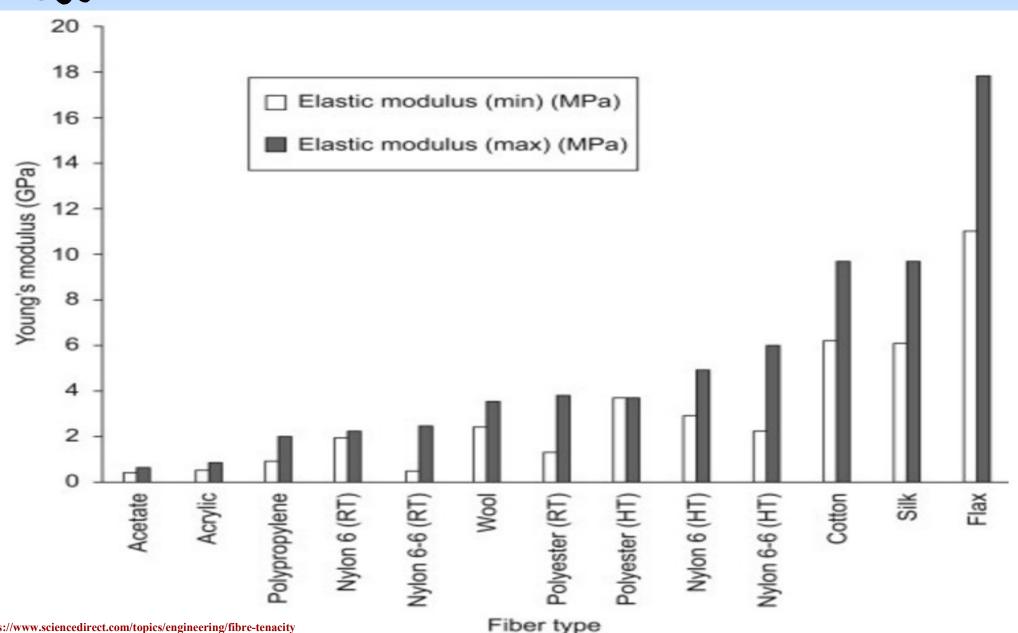






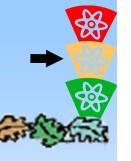








#### **Fibres**



+ anorganic

Chemica

**Natural** polysacharids proteins

Syntetic synthetic polymers PES, PP

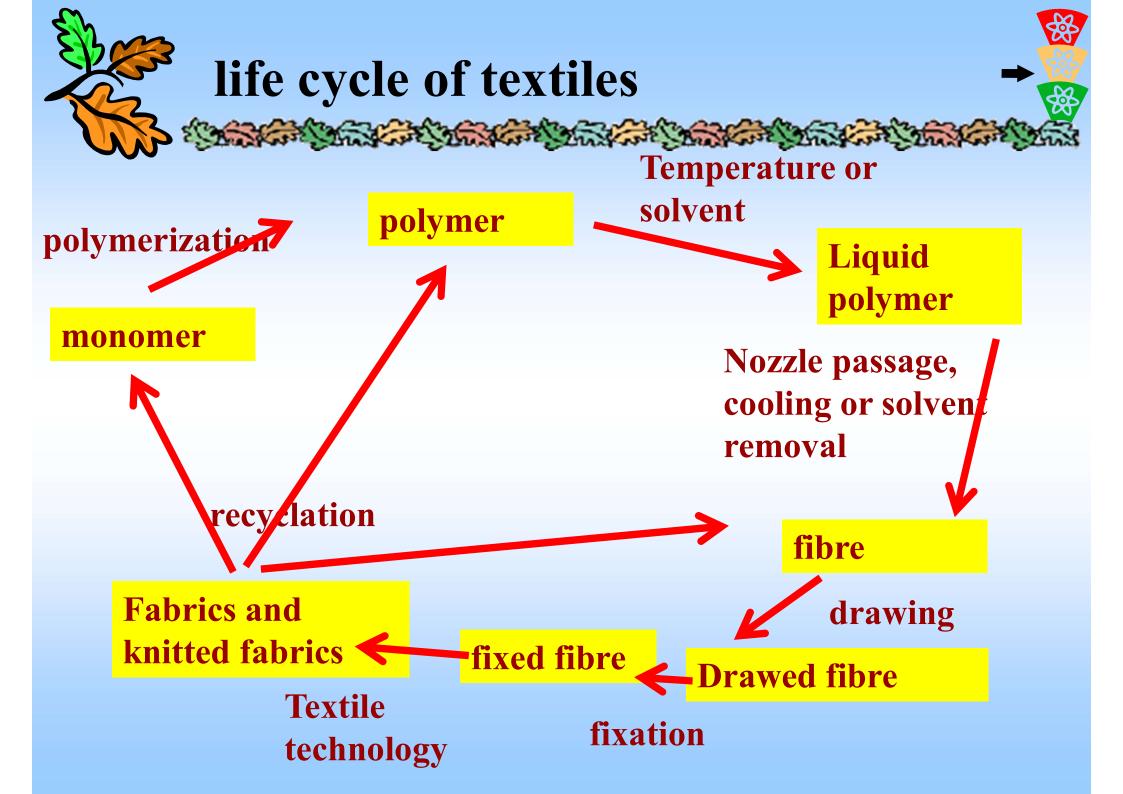
man-made fibres made from natural polymers



- natural polymers viscose
  - acetate

#### -syntetic polymers – polyamide

- polyester
- acrylic
- polypropylene
- polyuretane



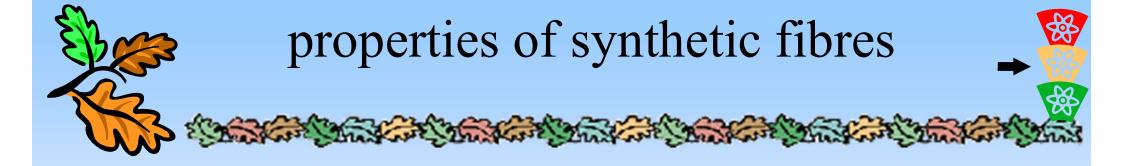


### properties of synthetic fibres

: not always pleasant to the touch, low absorbency wrinkling

: hydrophobicity — ability to bind oily dirt

: sensitivity to higher temperatures  $\rightarrow$  careful washing and ironing



Fibres made from synthetic polymers have a higher resistance to damage than fibres made from natural or regenerated natural polymers.

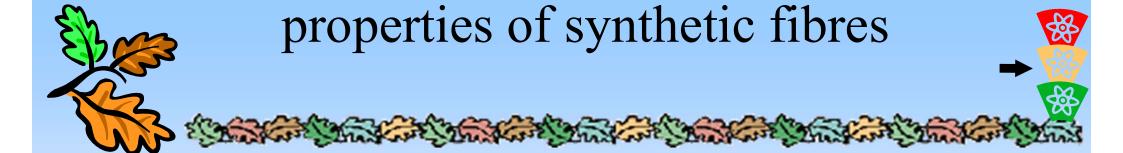
This higher resistance can be explained by the following hypotheses:

Non-polar stretches predominate in the macromolecules of synthetic fibres and non-polar bonds between atoms are difficult to cleave.

water penetrates the fibres only to a small extent, this is due to the compact structure of the fibre and its low hydrophilicity. If water does not penetrate the fibre, neither will chemicals dissolved in it. In hydrophilic fibres, water acts as a swelling agent, facilitating the entry of chemicals into the fibre. This principle is used, for example, when dyeing textiles.

#### properties of synthetic fibres

- •fibres have a simple chemical structure that can be expressed by a chemical formula. For natural fibres, the chemical formula is a simplification (or illusion) in addition to the "declared" building unit, many other units are present, often in trace concentrations. If such a complicated system comes into contact with an aggressive chemical, this chemical will attack the weakest link in the polymer chain and often it is the "undeclared" building unit. In general, the more varied the chemical composition of the polymer, the more likely it is that the polymer will be attacked.
- •The relatively high Tg temperatures prevent the diffusion of damaging chemicals into the fibres at normal temperatures, and damage is greatly accelerated once the Tg is exceeded
- •Note: Chemical modifications of fibres (copolymers) generally have lower resistance to chemical attack than unmodified fibres. An example of this is polyester, which is more sensitive to hydrolysis after modification and requires special refining methods. This is mainly due to the reduction of Tg and the 'diversification' of the chemical groups in the fibre. The chains are spaced apart by substituents the supramolecular structure is loosened.



Polyamide fibres are relatively poorly resistant to boiling solutions of mineral (inorganic) acids, whereas polyester fibres are generally sensitive to alkaline solutions (be careful when alkaline boiling PES/CO mixtures!).

The effect of oxidising agents on synthetic fibres is poorly studied, but in general it is true that fibres with a more polar structure (polyamides) are more easily degraded by strong oxidising agents.



Damage to synthetic fibres is caused by:
acids and alkalis
oxidation and reduction
solvents
exposure to high temperatures
radiation (e.g. UV) (resistance decreases in the following series:
PAN-PES-PA)

Note: Matting affects the lightfastness of the fibres. The crystalline structure of TiO2 plays an important role, which is negligibly damaging in the rutile form but very damaging in the anatase form. Titanium dioxide in a suitable form is used for targeted decomposition of organic materials - e.g. bathroom tiles can be self-cleaning - organic dirt is catalytically (by the action of TiO2) decomposed on them.

### Polyamide



Products: Polyamide fibre is more expensive to produce than polyester, so wherever possible, polyamide has been replaced by polyester. Mostly it is given only as an additive, except for underwear, hosiery and functional clothing.

**Properties:** 

Polyamides absorb dyes very well, they can be dyed at home with common cotton fabrics. They also like to soak up colour in the washing machine, so polyamide clothes should be washed strictly separated by colour, especially white clothes.

Washing gentle washing programme, hand wash or machine wash at 40 °C. Do not wring. Rinse well and do not use fabric softener. Iron at a low temperature. polyamide (PA) wash

between 30 °C and 60 °C Behaviour in wet Do not wring - risk of fractures conditions:

Excellent abrasion resistance, exceptional strength and ductility

### Polyamide



The polyamide fibre is temperature stable, so you don't have to worry about washing them at 60°C, it washes the sweat and dirt off the soles of the stockings well. Just be careful if you have silk stockings. They should be hand washed in a delicate detergent and not dried in direct sunlight. Wash stockings in a delicate laundry bag.

for women's hosiery and sports material, where washing and drying of the material after each use is necessary. is very elastic and high tensile and abrasion strength. Any symptoms of human skin sensitivity when wearing polyamide products are not caused by the properties of the fibre but by dyes, detergent residues, etc.

#### Chemické složení:

PENTAMID A = Polyamid 6.6

$$\begin{bmatrix} H & H & O & O \\ -N - (CH_2)_6 - N - C - (CH_2)_4 - C - \end{bmatrix}_N$$

PENTAMID B = Polyamid 6

$$\begin{bmatrix} \mathbf{O} & \mathbf{H} \\ -(\mathbf{C}\mathbf{H}_2)_5 - \mathbf{C} - \mathbf{N} - \end{bmatrix}_{\mathbf{N}}$$

PENTAMID AHT = Polyamid 4.6

$$\begin{bmatrix} -N - (CH_2)_4 - N - C - (CH_2)_4 - C - \\ | & | & | & | \\ H & H & O & O \end{bmatrix}_{N}$$

PENTAMID L = Polyamid 12

$$\begin{bmatrix} \mathbf{O} & \mathbf{H} \\ -(\mathbf{C}\mathbf{H}_2)_{11} - \mathbf{C} - \mathbf{N} - \end{bmatrix}_{\mathbf{N}}$$



## Polyamide (PA)



PA 6.6 - more ordered, more resistant to temperature (Tg, Tm... PA6+20°C), more chemically resistant...
PA 6.6 insoluble in DMF

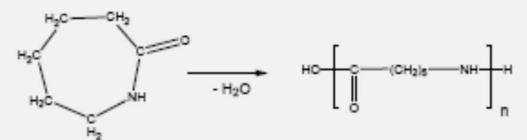
$$\frac{\begin{pmatrix} \mathbf{H} & \mathbf{H} & \mathbf{O} & \mathbf{O} \\ \mathbf{I} & \mathbf{I} & \mathbf{I} & \mathbf{O} \\ \mathbf{N} - (\mathbf{C}\mathbf{H}_2)_6 - \mathbf{N} - \mathbf{C} - (\mathbf{C}\mathbf{H}_2)_4 - \mathbf{C} \end{pmatrix}_n }{\mathbf{I} + \mathbf{I} + \mathbf{O} - \mathbf{C}}$$

Nylon 66

Number of carbons 6 (PA6) PA 10 = 10 Number of carbons

$$\begin{pmatrix}
\mathbf{H} & \mathbf{O} \\
\mathbf{N} - (\mathbf{CH}_2)_5 - \mathbf{C}
\end{pmatrix}_{n}$$

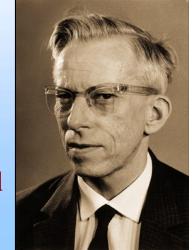
Nylon 6



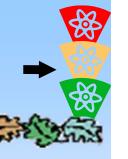
n = 200 s-Caprolactam

Monomer: kaprolactame Melting remperature 220 °C

Otto WICHTERLE (1913-1998) researched polyamides (silon)



## Polyamide 6.6



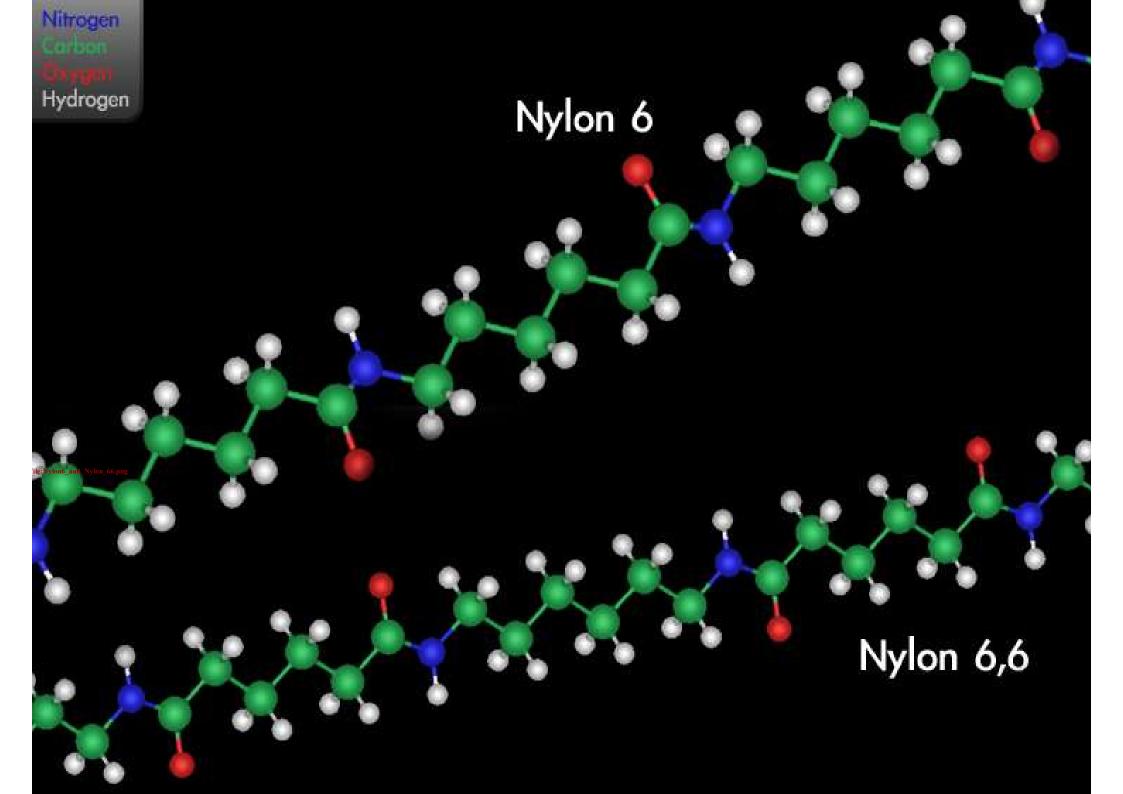
#### **Monomers**

$$H_2N - (CH_2)_6 - NH_2$$
  
hexametylendiamine

HOOC - (CH<sub>2</sub>)<sub>4</sub> - COOH adipic acid

#### **Polymer**

Melting temperature n= 50 až 80 260 °C





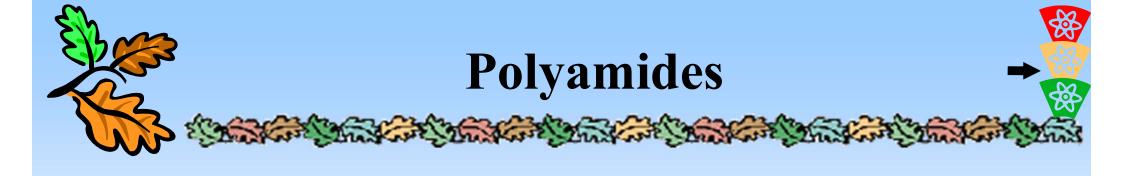




Nylon 6

$$CH_2$$
 $CH_2$ 
 $CH_2$ 
 $CH_2$ 
 $C = 0 \cdots H - N$ 
 $C = 0 \cdots H - N$ 
 $CH_2$ 
 $H_2C$ 
 $CH_2$ 
 $H_2C$ 
 $CH_2$ 
 $H_2C$ 
 $CH_2$ 
 $H_2C$ 
 $CH_2$ 
 $C$ 

POL14



#### **Chemical properties of polyamides**

**Action of acids** 

PA is less resistant to acids than to alkalis.

In acidic environments, hydrolysis of the amide bond occurs.

PA fibres are soluble in 85% HCOOH.

Action of alkalis PA fibres are virtually undisturbed.

Exposure to sunlight Fiber degradation, yellowing and loss of strength.



## Polyamide



#### Thermal damage

- Typical by ironing or by flash
- Microscopic identification: melted fibers
- Temperaure for ironing 160°C, melting point PA 6 215°C, PA 66 is it 260°C

Estimation based on viscosity of polymer solution (similar to cellulose)

Solvent: H2SO4 (95,6% - density 1,84g/cm³). 2 hours, 20°C - nondestructive damage - without light and oxygen

$$PPS = \left[\frac{248}{c} \cdot \sqrt{\frac{t}{t_0} - 1}\right] - 5$$

t ... Time of flow of solvent

t<sub>0</sub> ... Time of flow of polymer solution

c ... Polymer concentration in solvent [g/100ml]



PA ... Different polymerization degree (according the production technology)

Important is the monomer quantity – high influence on polymerization degree

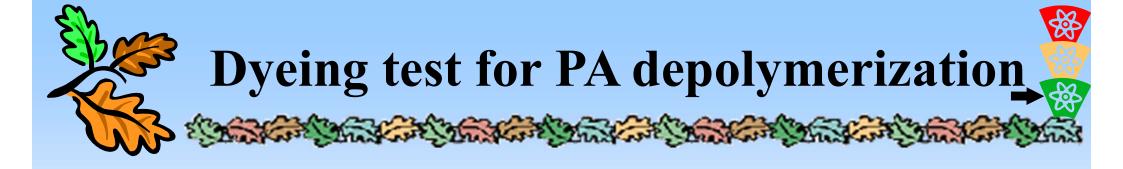
#### Example:

Unwashed PA 6 (7% of monomer): PPS =146

Washed PA 6 (monomer was wash off): PPS =170

After acid damage (boiling, 15 min, H2SO4 10%): PPS= 112

Quantity of monomer can be estimated by extract in in hot water



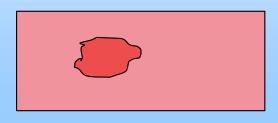
Acid damage – hydrolyses of PA

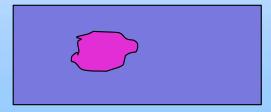
= increasing of NH2 groups quantity – they are on the one end of polymer chain (on the second one is COOH)

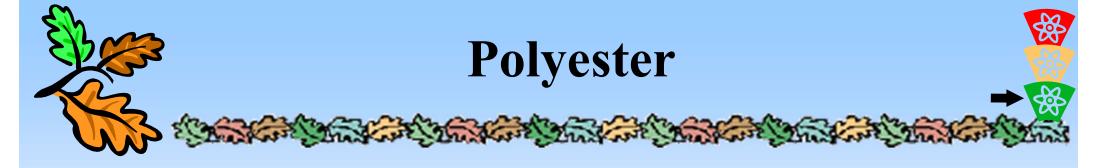
Damaged PA is more dyeable by acid dyes in low acide pH (in high acid: -NH- can be protonised and used for the dye sorption)

Damaged places - change of color deep (more and low red)

Dyeing with acide and disperse dyes – color differences ( red or violet) - The damaged places are more visible (disperse dye sorption is not sensitive to polymerization degree)







Products: Almost everywhere, especially in mixtures

**Properties:** 

It is especially appreciated by those who do not like ironing. When washing and ironing, it can withstand medium-high temperatures, but it tends to form wrinkles. It is therefore a good idea to wash it inside out. Due to static electricity, pet hair and all sorts of speckles often get caught on polyester.

Washing:

Polyester (PES) can be washed up to 60 °C depending on the type (see the label on the garment)

Don't buy fabrics with fine 'hairs' as these will instantly turn into pilling - fabrics with a smooth surface finish are safe.

ironed only through a wet cloth at a temperature up to 160 °C.

#### Polyester

#### **Chemical composition:**

the advantage of polyester fabrics is their low squishiness;

Polyester dulls scissors and needles faster.

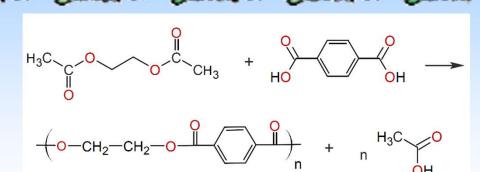
$$CH_3-O-C$$
 $CH_3-O-CH_2-CH_2-OH$ 
 $CH_3-O-CH_2-CH_2-OH$ 
 $CH_3-O-CH_2-CH_2-OH$ 
 $CH_3-O-CH_2-CH_2-OH$ 
 $CH_3-O-CH_2-CH_2-OH$ 
 $CH_3-O-CH_2-CH_2-OH$ 
 $CH_3-O-CH_2-CH_2-OH$ 
 $CH_3-O-CH_2-CH_2-OH$ 
 $CH_3-O-CH_2-CH_2-OH$ 
 $CH_3-O-CH_3-CH_3-OH$ 

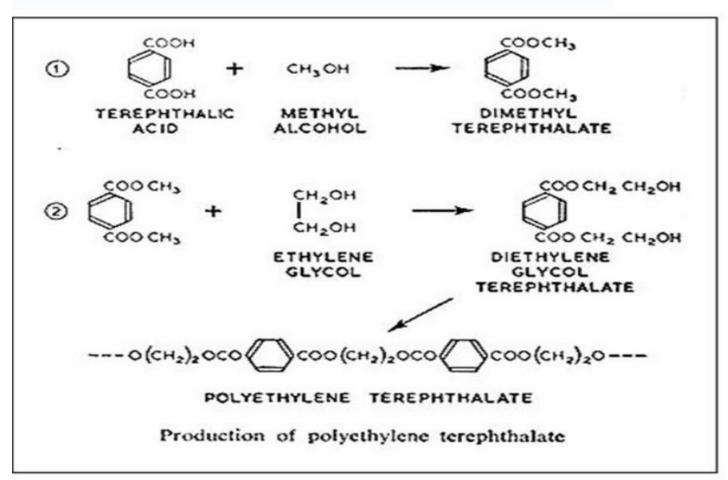
are highly resistant to light, weather and microorganisms and are easy to dry quickly. High strength, abrasion resistance and flexibility very good resistance to high temperatures good resistance to acids and oxidizing agents, less so to alkalis very low wettability → difficult dye uptake → fibres are anionically modified to increase dyeability

Don't buy fabrics with fine 'hairs' as these will instantly turn into wrinkles - fabrics with a smooth finish are safe.



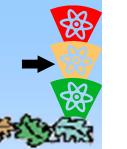
### Polyester







## Polyester



#### **Polyethylentereftalate**

Tg = 70 až 80 °C

$$T_{\rm m} = 260 \, {\rm ^{\circ}C}$$

$$\begin{bmatrix}
O & O \\
| & | \\
COCH_2CH_2O
\end{bmatrix}$$

$$n$$

$$\begin{array}{c|c} & & \\ & &$$



#### 



#### Počet methylenových skupin: (CH 2) n

- n = 2 (polyethylentereftalát) PET
- n = 3 (polytrimethylentereftalát) PTT (Tg= 55 °C, Tm= 228 °C)

$$CH_2$$
 —  $CH_2$  +  $CO$  +  $H_2$   $\xrightarrow{katal.}$  HOCH $_2$ CH $_2$ CH $_2$ OH

kyselina tereftalová + propandio → PTT

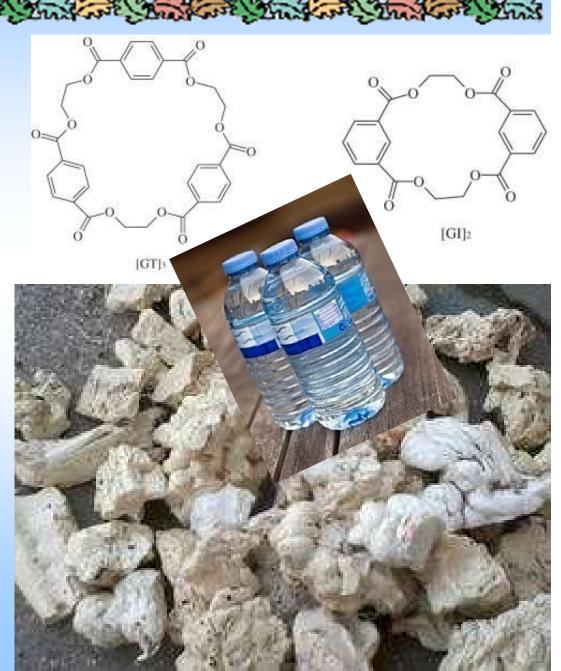


Polyethylene terephthalate - properties

The fibre is hydrophobic, highly crystalline and difficult to dye.

Dyeing: under pressure, at 130 0C

Problem: oligomers (e.g. cyclic trimer)





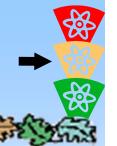
## Polyethylene terephthalate Alkaline hydrolysis

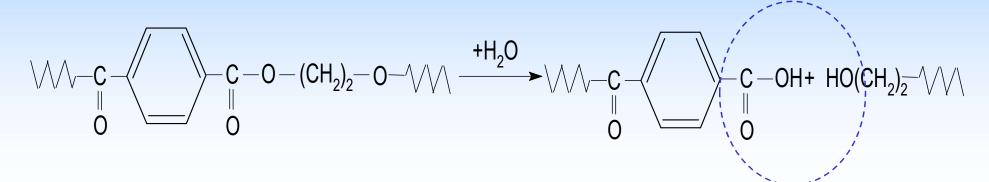
**■Depolymeration** 

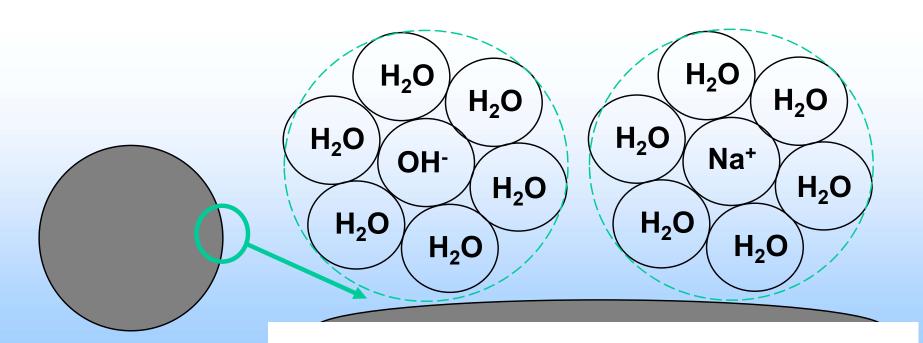
■Increase in the number of COOH and OH groups



## Alkalická hydrolýza PET









## Polyethylene terephthalate Alkaline hydrolysis

- ■Reduces fiber diameter runs from the surface to the fiber axis
- Amorphous parts degrade faster increases surface roughness
- ■Most common: NaOH
- Fiber mass decreases linearly with time when exposed to NaOH until eventual dissolution of the fiber,
- **■**Typical weight loss with this treatment 10%
- ■Conditions: NaOH 20 g.l-1, 45 min boiling, on 85%.

## Polyethylene terephthalate Alkaline hydrolysis

Roste smáčivost

■Příjemný omak

■pokles pevnosti vláken

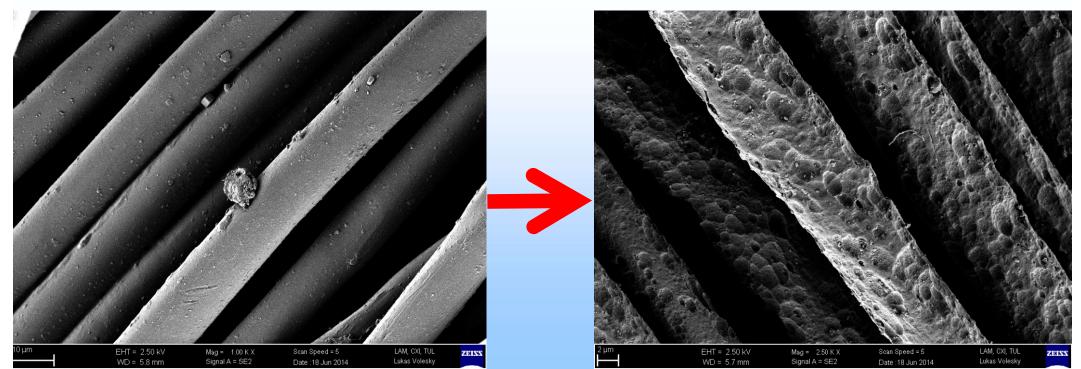
■Ekologicky problematické 20 g/l NaOH

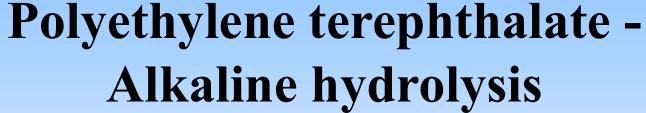
1:20, 98°C,

10,25,40,65,90,120,180 min

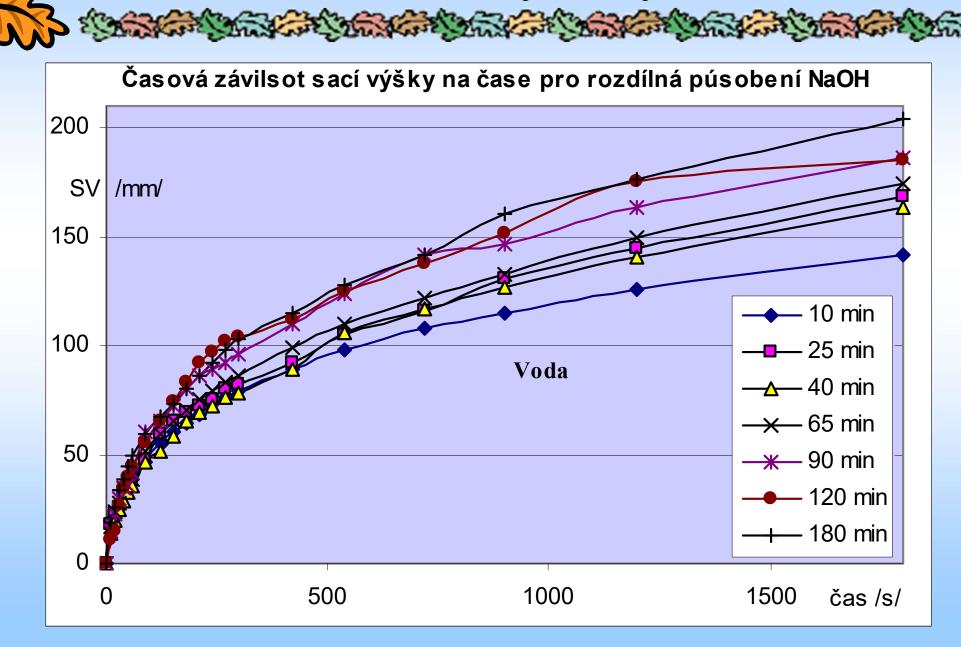
Rinsing

dryeing











Products: Sweaters, scarves, hats ... wool replacements

Properties: is lightweight, dries quickly, does not wrinkle, is

stain resistant and does not taste of moths. And a

cheap acrylic sweater, unlike a cheap wool

sweater, doesn't bite.

Washing: acrylic, like wool, is more susceptible to damage (pulling) when wet - so do not wring or dry hanging. It can shrink if washed in too hot water.

Iron through a wet cloth



### Polyacrylonitrile (acrylic) fibers →



## **Chemical composition:**

Acrylic fabrics, including knits, wrinkle very readily and also easily build up a static charge. And one more disadvantage compared to wool: acrylic heats less and stinks faster

- > by increasing the temperature, the fibres soften
- > considerable resistance to acids, oxidizing agents and weak alkalis, less so to concentrated NaOH solutions
- $\gt$  low wettability  $\to$  fibres are difficult to accept dyes  $\to$  fibres are anionically modified to increase dyeability
- ➤ Modacrylic fibres copolymers with PAN content less than 85%



### Polyacrylonitrile (acrylic) fibers



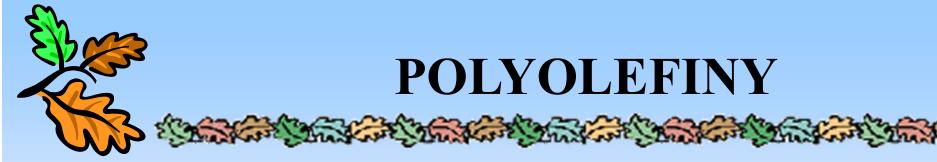
Polyacrylonitrile - properties

PAN fibers - very good acid resistance (except for sulfuric and nitric acids)

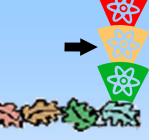
Medium resistance to alkalis.

Decomposes in hot concentrated alkalis.

**PAN** fibres - resistant to light.



### **POLYOLEFINY**



Polyethylene, polypropylene

Polyethylene fibres 0,95–0,96 g/cm<sup>3</sup> Polypropylene fibres 0,90-0,91 g/cm<sup>3</sup>

lightest fibres, floats on water

$$-\text{CH}_2-\text{CH}_{\frac{1}{n}}$$
 $-\text{CH}_3$ 

$$+CH_2-CH_2+$$

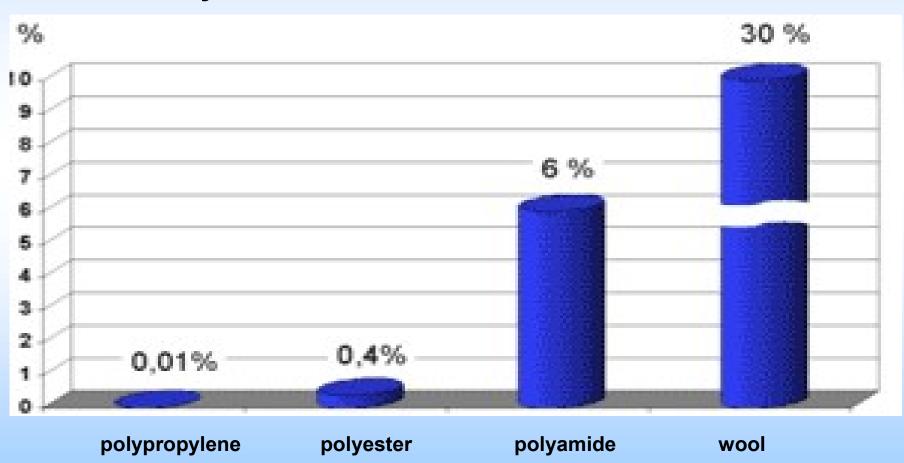


### **POLYOLEFIN**



### Humidity

#### Water sorption





### Polypropylen



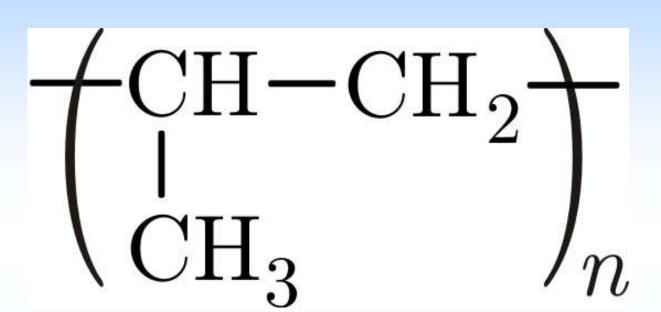
Vlastnosti:

It has the properties necessary for the production of functional underwear: it is the strongest, lightest, also the warmest and most flexible of the synthetic fibres. It does not cause allergic reactions, has a high abrasion resistance (2.5 times higher than cotton), only polyamide fibres have a higher resistance, it almost does not absorb water - it has 10 times less water absorption than polyester - but it wicks water well. It is hydrophobic.

Washing and ironing: low temparature



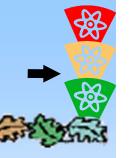
### Polypropylene



minimal wettability → very poor dyeability
excellent stability against chemicals
fibres are lighter than water
textile industry, technical purposes - ropes, tarpaulins



# 





$$OH - R - OH + OCN - R' - NCO \longrightarrow \begin{bmatrix} C - N - R' - N - C - O - R - O \end{bmatrix}_{n}$$

diol diisocyanatane

Polyurethane fibres - very elastic, UV resistant.



### **POLYURETANE**

Products: Lycra is the trade name for Du Pont's elastane. It is not used alone, but is combined with other materials.

#### **Properties:**

The unique ability of the fibre to stretch (at least three times) and return to its original state improves the properties of all types of clothing in which it is contained. The elasticity of Lycra fibres allows for an excellent fitting of clothing without impeding movement. Clothes with Lycra retain their shape, do not form creases, do not cause abrasions, blisters and blisters and are characterized by increased wrinkle resistance.



### **POLYURETANE**



**→** 

1,6-hexamethylendiizokyanate

1,4-butandiol butylenglykol

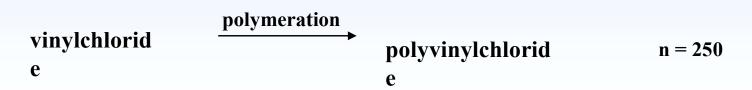
polybutylenglykolhexamethylendiizokyanate

low wettability → difficult to dye

good resistance to acids and alkalis, fibres dissolve in concentrated mineral acids and formic acid; easy solubility in dimethylformamide

sportswear and linings

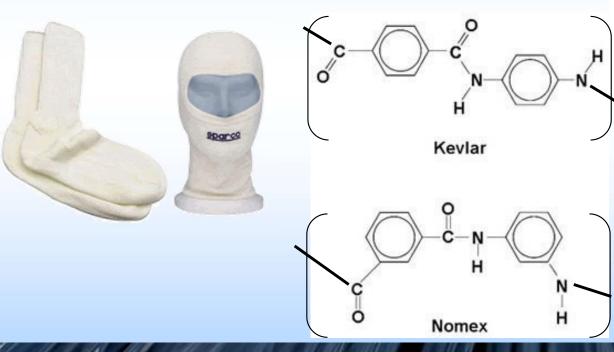


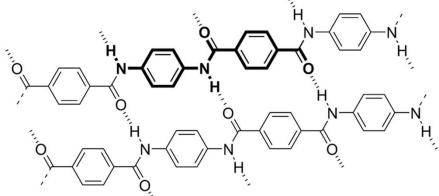


- > flame retardant fibres
- ➤ high resistance to alkalis, oxidizing and reducing agents, resistant to
- > Concentrated acids; swells in organic solvents,
- dissolves in acetone (cannot be chemically cleaned)
- > already at low temperatures (70 ÷ 75 °C) they deform and precipitate
- > production of medical underwear with antirheumatic effect

### Special fibres

### Glass, Teflon, Kevlar, Nomex... extreme properties









I can't believe it!

My own son wearing synthetic clothing!



-From natural polymers - Viscose

- acetate



Výrobky:

výrobků, které se mají podobat přírodnímu hedvábí, ale nesmějí být příliš drahé (tkanina na halenky, šatovky a podšívky). Viskózové látky jsou vesměs velmi příjemné na nošení, měkké, savé, splývavé a chladivé.

#### Vlastnosti:

Za průměrnou bavlnu se často platí dvojnásobek a za vlnu čtyřnásobek ceny obyčejných viskózových vláken. Vysoká absorbce potu a stálobarevnosti. Je to výborně savý materiál, snadno barvitelný

Praní:

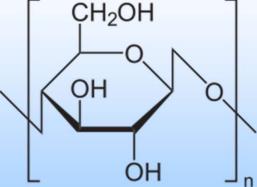
chemické čistění nebo šetrný prací program, ruční praní nebo praní v pračce při 30 - 40 °C. Vyhněte se předepírání a namáčení. Při vyšších teplotách se sráží



Chování za mokra: viskózové vlákno dosahuje v suchém stavu jen asi 80-90% pevnosti bavlny a za mokra klesá na polovinu, hodně se mačká, snadno se nošením prodře a některé látky mají tendenci se srážet. takže aby se oblečení nevytahalo, nesmí se ždímat (jen vymačkat) a sušit pověšené. Platí to především pro úplety, tkaniny jsou k tomu méně náchylné.

Žehlení: žehlení by mělo být při nízkých teplotách

Chemické složení:



Citlivé na: Mimo jiné nejsou odolná proti biologickým vlivům

Stabilní vůči: ?

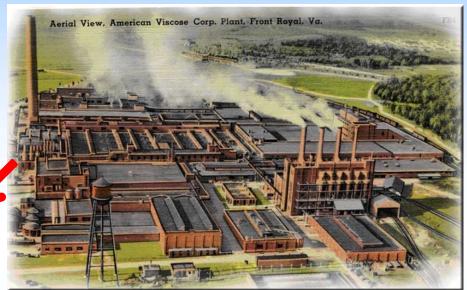


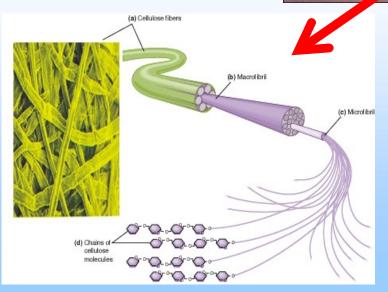
### Viscose

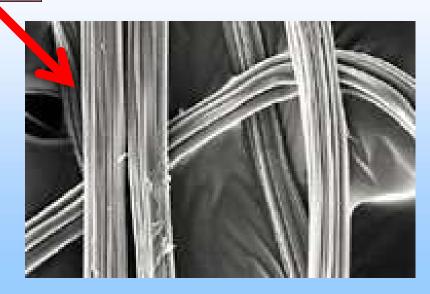


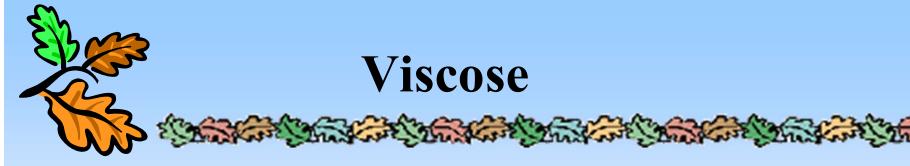




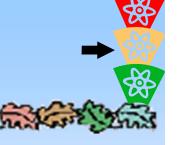








### **Viscose**



výroba – z celulózy:

alkalicelulóza – dlouhý řetězec celulózy se zkracuje – PPS klesá na 300÷600

• alkalizace : cel-OH + NaOH ---- cel-ONa + H<sub>2</sub>O

xanthogenát celulózy

$$S = C - \frac{\text{O-cel}}{\text{S-Na}}$$

• xanthogenace : cel-O.Na + CS<sub>2</sub>

CS<sub>2</sub> – sirouhlík

• zvlákňování a koagulace 2 xantogenát + H<sub>2</sub>SO<sub>4</sub>

$$\longrightarrow$$
 Na<sub>2</sub>SO<sub>4</sub> + 2 CS<sub>2</sub> + 2 cel-OH

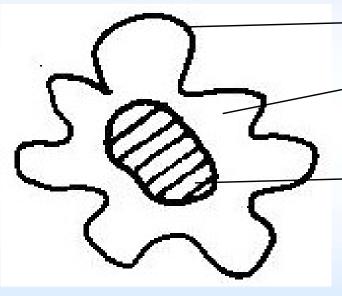
Celulóza (viskóza)

# Viscose

production - from cellulose : alkalization

xanthogenation (reaction with sulfur carbon)

Coagulation and spinning



skin (cuticle) - high crystallinity

bark (35% of fibre mass) well oriented crystallinity  $\rightarrow$  well dyeable

pith (65 % of fibre mass) less oriented crystallinity → less dyeable

fibre - up to 60 % amorphous areas

- properties similar to those of cotton fibre
- $\Leftrightarrow$  more sensitive to water  $\rightarrow$  strong swelling
- **❖** lower resistance to alkalis → swelling and reduced wet strength
- ❖ yellowing at higher temperatures and decomposition at T = 180 ÷ 200 °C



#### **Special types of viscose:**

High-tenacity viscose fibres - strength is achieved by increasing the degree of elongation

modal fibres - CMD - high orientation of cellulose molecules → high wet modulus; properties approach those of cotton, softer feel polynosic fibres - higher wet modulus, higher strength, more brittle, more sensitive to abrasion

HWM (High Wet Modulus) fibres - properties close to cotton, higher PPS, higher crystallinity, higher ductility, medium wet modulus



### Lyocel - Tencel



**Products:** 

it is a popular material mainly for underwear,

T-shirts or towels. Bed clothes

**Properties** 

Lyocell (Tencel is the trade name for lyocell) is produced using a method that is environmentally friendly. it is produced by dissolving cellulose in Nmethylmorpholine-N oxide - NMMO

It has a higher absorbency than cotton, does not shrink and is softer and softer than quality mercerized cotton. Almost wrinklefree higher dry and wet strength, lower dry and wet elongation

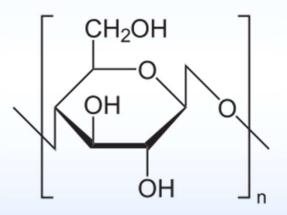
very good affinity to dyes (colour brilliance), resistance to alkalis, complete biodegradability, washable at 60 °C, Disadvantages: low elasticity (squishiness) and low acid resistance



## Lyocel - Tencel



#### **Chemical composition:**



**Sensitive to:** 

acides

fibre	Lyocell	viscose	polynosic	Cu- ammonia	cotton
Dry strength (cN/tex)	42	22	37	11	22
Dry elongation (%)	15	22	12	7	8
Wet strength (cN/tex)	36	12	28	9	27
Wet elongation(%)	17	27	12	6	14
Moisture (%)	68	95	62	100	50



COPPER-AMMON fibre is produced by dissolving cellulose in cuoxam (Schweitzer's reagent) - [Cu(NH3)4](OH)2 It behaves similarly to cotton with respect to chemicals, however, its resistance is lower, however, it is resistant to organic solvents.



### derivatives of cellulose



#### **Cellulose acetate**

Vzniká působením anhydridu kyseliny octové

Cel. – OH + 
$$(CH_3CO)_2O$$
 — cel. – O – CO –  $CH_3$ 

Využití – výroba acetátového hedvábí

### **Cellulose nitrate**

Nitration of cellulose by mixtures HNO<sub>3</sub> a H<sub>2</sub>SO<sub>4</sub>

Cel.- OH 
$$\longrightarrow$$
 cel. - O - NO<sub>2</sub>

**Application - coatings** 



**Products:** Acetate fibre has a high gloss, which is why it is mainly used to make satins, taffetas, brocades, but also knits and lace. Acetate linings are most often found in shops - they are more expensive than polyester linings, but are much more comfortable to wear. Test: acetate dissolves in acetone, polyester does not

**Properties:** 

even lighter than natural silk, resists stains better and wrinkles a little less.

**Washing:** Dry cleaning or gentle washing programme, hand wash or machine wash at 40 °C. Avoid pre-washing and soaking.



Chování za mokra: Po namočení je acetát náchylnější k poškození

#### Žehlení:

#### Chemické složení:

z celulózy pomocí esterifikace : cel-OH +  $CH_3COOH \longrightarrow cel-O-CO-CH_3$  acetylcelulóza +  $H_2O$  triacetát je rozpustný v dichlormethanu  $CH_2Cl_2$ ; acetát v acetonu  $CH_3-CO-CH_3$ 

Děkuji za pozornost



I finally found something

I can do with my short arms...