Unit - Chemistry of Garments: Animal Fibres

Alpaca, Angora, Byssus, Camel hair, Cashmere, Catgut, Chiengora, Guanaco, Llama, Mohair
Pashmina, Qiviut, Rabbit, Silk, Sinew, Spider silk, Wool, Vicuña, Yak

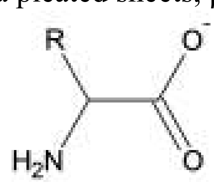
Silk

Silk can be obtained from the cocoons of several types of caterpillar or silkworm, but it is now the Chinese silk moth (mulberry silkworm *Bombyx mori*) reared in captivity that is mainly cultivated. See the Zanzibar Tribal Art web site for an explanation and diagram of the life cycle of the various silkworms.

YouTube video clip of Silk factory in Beijing
Natural silk is one of the strongest textile fibres, which are accounted for by the stretched-out molecular form. Silk (78% protein) is much stiffer than wool in spite of both being proteins made from amino acids chains. Silk fibres have fine draping qualities and are naturally crease-resistant and bring about a warm feel to the skin.

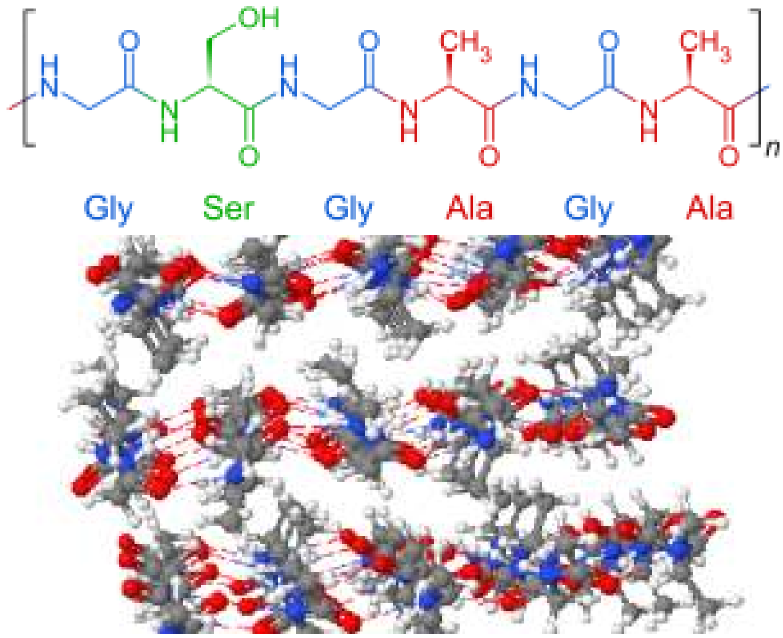
Of the 3-4000 metres of fibre in a cocoon, laid out as a figure of eight by the movement of the head of the pupae, less that one third is generally usable with much of the remainder being processed separately.

Silk emitted by the silkworm consists of two main proteins, sericin and fibroin, fibroin being the structural center of the silk, and serecin being the sticky material surrounding it. Fibroin is largely made up of the amino acids Gly-Ser-Gly-Ala-Gly-Ala and forms beta pleated sheets, β-keratin.



R = H, glycine; R = CH_3, alanine; R = CH_2OH, serine

Hydrogen bonds form between chains, and side chains form above and below the plane of the hydrogen bond network.



fibroin protein in silk

The amino acid compositions of the silk proteins are shown below. B. mori silk fibroin contains a high proportion of three α-amino acids, glycine (G; Gly, 45%, R=H), alanine (A; Ala, 29%, R=CH_3), and serine (S; Ser, 12%, R=CH_2OH), in the approximate molar ratio of 3:2:1, respectively. Tyrosine, valine, aspartic acid, glutamic acid, etc. make up the remaining 13%.

Reference: Fraser, R.B.D. and MacRae, T.P. Conformation of Fibrous Proteins and Related Synthetic Polypeptides, Chapter 13. Silks. Academic Press: New York, 1973; 293-343.

Silk protein composition, percentage of amino acids found

symbol	Amino acid	Fibroin	Sericin
G	(glycine)	45	14
A	(alanine)	29	5
S	(serine)	12	33
Y	(tyrosine)	5	3
V	(valine)	2	3
D	(aspartic acid)	1	15
R	(arginine)	1	3
E	(glutamic acid)	1	8
I	(isoleucine)	1	1
L	(leucine)	1	1
F	(phenylalanine)	1	1
T	(threonine)	1	8
C	(cystine); half	0	0
H	(histidine)	0	1
K	(lysine)	0	4
M	(methionine)	0	0
P	(proline)	0	1
W	(tryptophan)	0	0

The high proportion (45%) of glycine, which is a small amino acid, allows tight packing and the fibers are strong and resistant to breaking. The tensile strength comes from the many interseeded hydrogen bonds, and when stretched the force is applied to these numerous bonds and they do not readily break.

Silk is one of the strongest natural fibers but loses up to 20% of its strength when wet. It has a good moisture regain of 11%. Its elasticity is moderate to poor: if elongated even a small amount, it remains stretched. It can be weakened if exposed to too much sunlight. It may also be attacked by insects, especially if left dirty.

Silk is a poor conductor of electricity and thus susceptible to static cling. It is resistant to most mineral acids, except for sulfuric acid, which dissolves it. It is yellowed by perspiration.

Note:
To produce 1 kg of silk, 104 kg of mulberry leaves must be eaten by 3000 silkworms. It takes about 5000 silkworms to make a pure silk kimono. Most of the pupa are killed in the process since it is not practical to cut open the coccoon without damaging the silk. A small proportion is kept for further breeding.

The following provides some basic information on how silk is made. The commercial process of silk making is both complex and labour intensive.

- **Sericulture** - cultivation of the silkworms.
- **Hatching the Eggs** - the female deposits 300 to 400 eggs at a time.
- The Feeding Period - for about six weeks the silkworm eats chopped mulberry leaves almost continually.
- **Spinning the Cocoon** - this is done over a 3 to 8 day period. The fibroin is secreted by two salivary glands and forced through openings called spinnerets. A second set of glands secretes the sericin.
- **Reeling the Filament** - the cocoon is treated with hot air, steam, or boiling water and the silk is then unbound by softening the sericin and then delicately and carefully unwinding or 'reeling' the filaments.
- **Types of Silk** - raw silk (still containing the sericin) is twisted into a strand sufficiently strong for weaving or knitting. This process of creating the silk yarn is called 'throwing'

Chem and Eng News, 12 Sept 2011, p 20.
Researchers at the Smithsonian Institution have developed a way to estimate the age of ancient silk from just a piece of fluff from priceless textiles. The new mass spectrometry-based technique requires a silk sample size that is signficantly smaller than what is needed for successful carbon-14 dating, the only other scientific method that can date silk, explains Mehdi Moini, a conservation chemist at the Smithsonian's Museum Conservation Institute. Moini developed the technique with Kathryn Klauenberg and Mary Ballard (Anal. Chem., 2011 DOI:10.1021/ac201746u). Silk is composed of intertwining strands of protein extruded by a silkworm and has been used as a textile for some 2,500 years in flags, tapestries, carpets, and clothing. The Smithsonian team examined aspartic acid residues in silk protein and found that, over time, aspartic acid racemizes, changing from the L form to the D form. They discovered that by measuring the L-to-D ratio, the age of the textile could be determined.

Spider Silk
It has been shown possible to extract the spider silk gene and use other organisms to produce the spider silk. In 2000, Canadian biotechnology company Nexia successfully produced spider silk protein in transgenic goats that carried the gene for it; the milk produced by the goats contained significant quantities of the protein, 1-2

grams of silk proteins per liter of milk.

A Bullet Proof Skin was recently produced from spider web obtained from transgenic goats!

Wool

Wool is the textile fiber obtained from sheep and certain other animals, including cashmere from goats, mohair from goats, qiviut from muskoxen, vicuña, alpaca, and camel from animals in the camel family, and angora from rabbits.

Wool has several qualities that distinguish it from hair or fur: it is crimped, it is elastic, and it grows in staples (clusters). The term wool is usually restricted to describing the fibrous protein derived from the specialized skin cells called follicles in sheep.

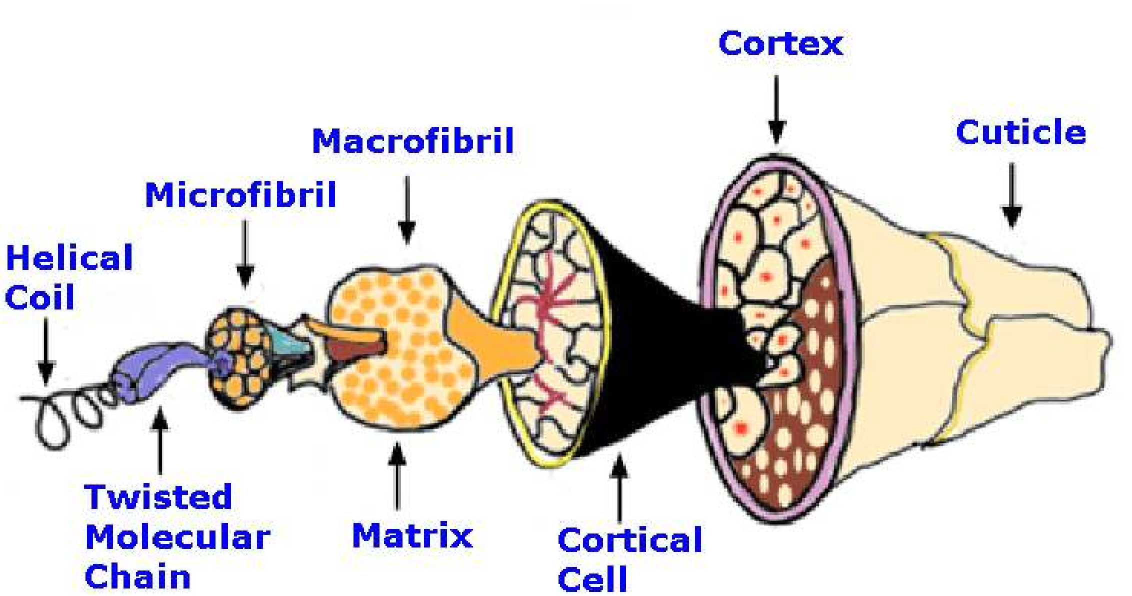
Sheep grazing at Lyonville, Victoria, Australia

See the YouTube video clip on shearing merino sheep in NSW, Australia

Wool and hair are fibres of protein (keratin), that have a very complicated structure consisting of dead cells, which emerge from the hair follicles and are much overlaid with grease. The fleece sheered during the warm season contains only about 43-50% of wool by weight. The rest are the oils, fats, moisture and dirt.

The textile properties of wool have been appreciated for more than 12,000 years. For example, among its many qualities are:

- Wool is insulating. It insulates against the cold as well as heat, thanks to the quantity of air that is trapped in its fibers. Wool keeps us warm during the winter and is pleasant to wear during the summer.
- Wool is an excellent regulator of humidity : it can absorb up to 30% of its weight in humidity without feeling damp or breaking. This hydrophilic property of wool allows it to breathe.
- Wool has excellent elasticity and memory and of all the natural fibres it is the most resistant to creasing. Thanks to these properties, garments made from wool keep their shape and resist wrinkling.
- Wool has a natural affinity for dye : it is a textile fiber that is easy to dye.
- Wool is naturally fire retardant.
- Additionally, wool is a natural resource : renewable and ecological.



Structure of wool

The outside of wool has a protective layer of scales called Cuticle cells that overlap each other like roof tiles. The interior of the wool fiber is called the Cortex and this makes up about 90% of the fiber.
Cortical Cells have a complex interior structure that includes:

Twisted Molecular Chain and Helical Coil

These cells are protein chains that are coiled in a helical shape like a spring. The chains are stiffened by hydrogen and disulfide bonds, linking each coil of the helix, helping to prevent it stretching. Though the helical coil is the smallest part of the fibre this little spring gives wool its flexibility, elasticity and resilience; helping wool fabric keep its shape and remain wrinkle free.

Microfibril

These cells mke up the units, lying inside the Matrix. The microfibrils are like the steel that is embedded in concrete to provide the strength and flexibility. The microfibrils contain three right-handed helices wrapped around each other in a left-handed coil where they are held together by more H-bonds and sulfur bridges (protofibril). Nine of these protofibril coils cluster around two more so that the microfibril contains a total of eleven coils each consisting of three α-helices.

Matrix

The matrix consists of high sulfur proteins. This makes the wool absorbent because they attract water molecules. Wool can absorb up to 30% of its weight in water and can also absorb and retain large amounts of dye. The Matrix region is responsible for wool's fire resistance and antistatic properties.

Macrofibril

Inside the cortical cells are the macrofibrils that are made up of bundles of hundreds of the even finer filaments (the microfibrils). These are surrounded by the matrix region.

Fibrous keratin molecules supercoil to form a very stable, left-handed superhelical motif to multimerise, forming filaments consisting of multiple copies of the keratin monomer. See the structure of proteins by Donald and Judiith Voet, and Charlotte Pratt.

Amino acid composition of keratin fibres

Component	**Merino Sheep Wool**		**Human Hair**		**Mohair**	
	g 100 g^{-1}	mmol g^{-1}	g 100 g^{-1}	mmol g^{-1}	g 100 g^{-1}	mmol g^{-1}
Cys	12.02	1000	17.08	1422	9.7	808
Glu	14.41	980	13.02	885	15.52	1055
Ser	9.66	920	8.94	851	7.83	745
Gly	5.25	700	3.84	512	4.84	645
Leu	8.26	630	6.08	464	8.7	672
Pro	6.79	590	8.67	753	6.41	557
Arg	9.58	550	8.29	476	8.53	490
Thr	6.54	550	6.45	542	5.74	482
Asp	6.65	500	5.52	425	7.24	544
Ala	4.1	460	3.07	345	4.03	452
Val	5.38	460	5.73	490	7.76	663
Tyr	5.25	290	2.28	126	3.51	194
Ile	3.41	260	2.78	212	3.57	272
Phe	3.8	230	2.36	143	4.04	245
Lys	3.22	220	2.6	178	3.26	223
Trp	1.43	70				
His	1.02	66	0.96	62	1.09	70
Met	0.52	39				
Hyl	0.16	10				
Ammonia	1.2	750	1.28	797	1.27	793
N%	16.35		16.5		16.6	
S%	3.65		5.1		3.0	

Reference: N.H. Leon, J. Society of Cosmetic Chemists of Great Britain, 23, 427-445 (1972)

The ability of the highly wound structures to unwind, even to the extent of breaking the H-bonds, is what allows wool and hair to stretch. Normally the shape is restored when the tension is released and the H-bonds then reform. Note that a *permanent wave* involves stretching and breaking the S-bridges so that when the bridges reform they are in different positions.

- In 2010/2011 75 million sheep were expected to be shorn in Australia and production was estimated to be 350 million kg of greasy wool.
- Australia is the world's largest producer of wool, producing 21.5% of the world's greasy wool in 2008.
- While Australia produces more wool than any other country, China has the largest sheep population.

Note that fingernails and claws are a form of α-keratin as well. The Guinness World Book of Records for 2012 has just announced a winner for the longest fingernails .....

Comparison between silk and wool.

One difference between silk (β-keratin) and wool (α-keratin) is that in silk the amino acids, glycine, alanine and serine are quite small with no bulky side-chains. When combined together they do not form helices and instead lie on top of each other to give pleated sheets of linked amno acids with the glycine appearing on only one side of the sheets. The sheets then stack on top of each other.

This planar structure is felt when you touch the smooth surface of silk. Silk is less extensible than wool because its polypeptide chains are all nearly fully extended already. The limited flexibility comes from the weak interaction between the sheets that allows one sheet to slide over another by breaking the (loose) H-bonds.

Assignment
Hoe does the fibre structure of silk and wool influence the properties of the final textile. (Include things like ability to maintain shape, effect of moisture, etc.)

Acknowledgements.
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