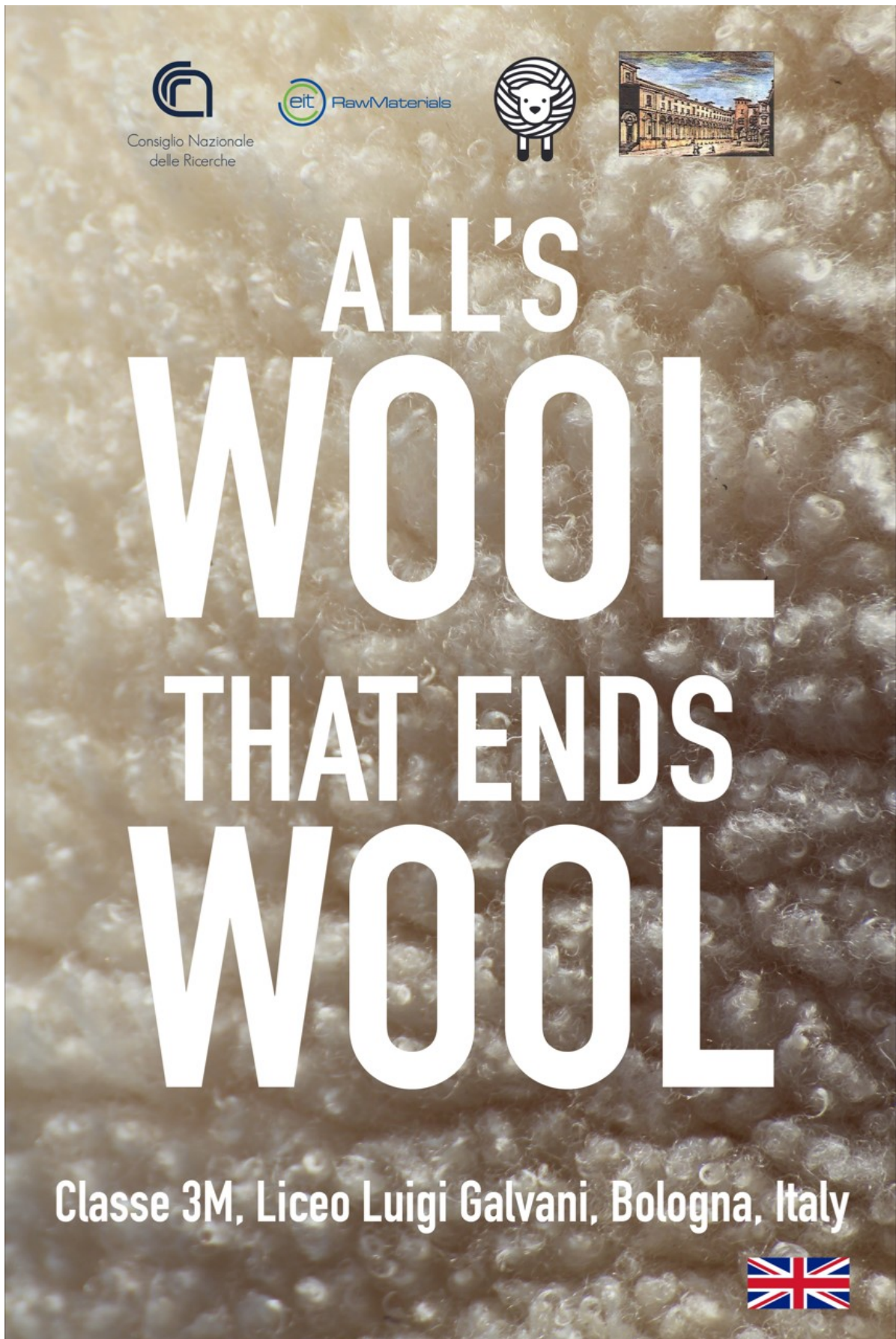






Appendix 1 – All's wool that ends wool




Consiglio Nazionale
delle Ricerche


 eit RawMaterials





ALL'S WOOL THAT ENDS WOOL

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PREFACE

The eBook "All's wool that ends wool" was created for the project RawMaterials@School of the European organization EIT RawMaterials. This digital book promotes scientific culture among teenagers between 14 and 19 years old. It is a toolkit consisting of theoretical and practical material about innovative uses of wool wastes from the dairy industry. The problem is that these wastes are normally burnt to be disposed of, so they release harmful gases.

Before the creation of the eBook two lessons held by scientist Annalisa Aluigi (ISOF-CNR, Bologna) were attended in order to acquire the knowledge needed to carry out the project. In the first lesson she introduced the basic information about the topic, whereas the second time we went to the laboratory and watched her do the experiments.

The purpose of our project is to report our experience, enabling other students and their teachers to learn the subject and therefore repeat the experiments.



1 – WOOL HISTORY

Wool has always proved its extreme versatility in the throughout history. The activity of sheep breeding, in fact, started around 10000 BC with the sole aim of producing meat. Humans began to consume milk and dairy only in 5500 BC, when a genetic mutation made it possible for the gene responsible for lactase synthesis to pass on to the next generations. As for wool production, the most ancient records proving its employment date back to 3000 BC, when it substituted fur in clothes. This happened thanks to the introduction of some of the first spinning techniques (Gallery 1.1).



"Egtved girl", 1370 a.C., Copenhagen, National museum of Denmark. The girl wore woollen gear, consisting of a short tunic and a skirt.



"Pazyryk Carpet", 5th century BC, Saint Petersburg, The State Hermitage Museum. It is the world's oldest carpet, woven with the technique of the double knot and dyed with bright hues.



"Huldre Fen's wife", 2nd century BC, Copenhagen, National museum of Denmark. The scarf and the skirt the woman wore were made of wool.

Gallery 1.1 – Some of the most ancient woollen artifacts.

Wool was essential on the Mesopotamian market, as demonstrated by some fragments of a Babylonian document, the Paleo-Babylonian Scholastic Prism. This written account reports trade involving wool and, even though it is highly damaged (Gallery 1.2), it is still possible to read some terms of a commercial contract. *"1 talent of wool of the foreign land, of good quality – [its silver (is) 1 shekel] for 6 minas (of wool) – ... (of) goat, f[rom] PN] Ur-[...], the merchant, has received. The half^o of the silver (value of the wool) in the second month, its (further) half^o [he will give (back)^o] ... (unknown number of lines lost)."*



Detailed study

Lactase

Lactase (or β -galactosidase) is the enzyme responsible for hydrolysing lactose, which is broken down into glucose and galactose. These are two simple sugars that humans can digest. The enzyme, coded by the gene LCT on chromosome 2 in the position 2q21.3 (Figure 1), was exclusively produced during childhood and it used to disappear in adulthood until the 6th century BC. Since 5500 BC, however, a genetic mutation made it possible for humans to continue the synthesis of lactase throughout their lives. This has been a considerable evolutionary advantage, since it has allowed us to introduce non-human milk and dairy in our diet even after childhood.

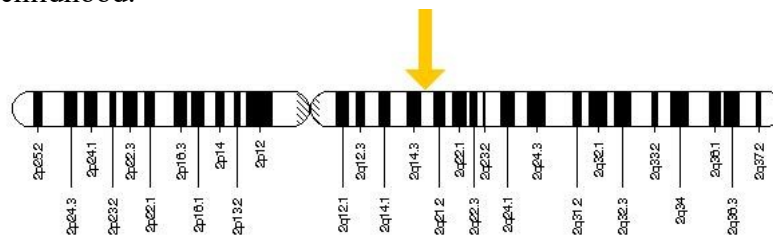
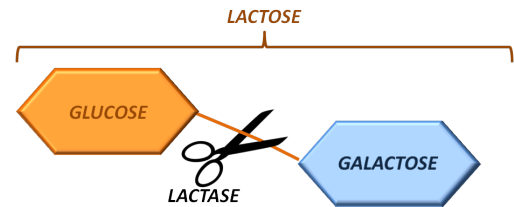


Figure 1

Nowadays this gene is active in around 70% the adult population in the western world, who is therefore capable of assimilating lactose. In Asia, on the other hand, the situation is diametrically opposite, but since Asian people do not traditionally consume milk or dairy, they are not really disadvantaged. The gene of lactase and a genetic polymorphism, responsible for lactase persistence, have been recently identified on chromosome 2, in the position -13910 of the gene.

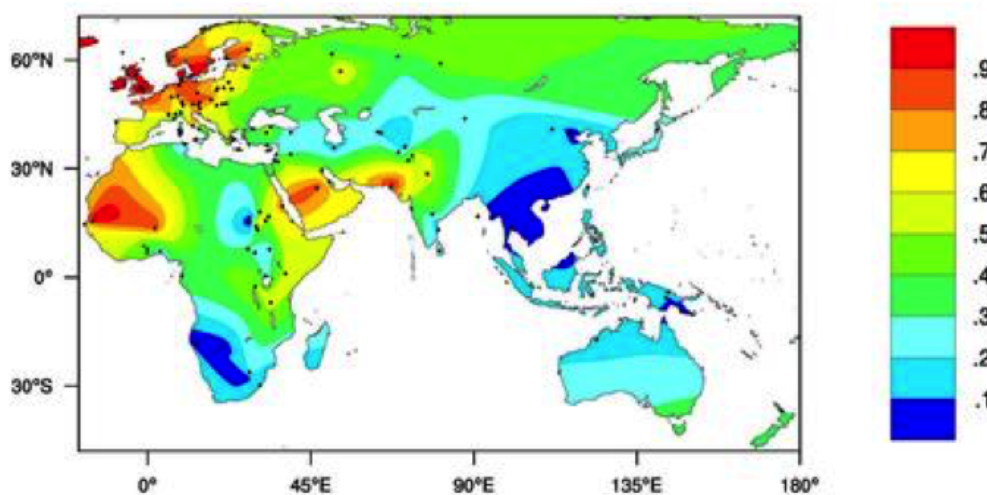
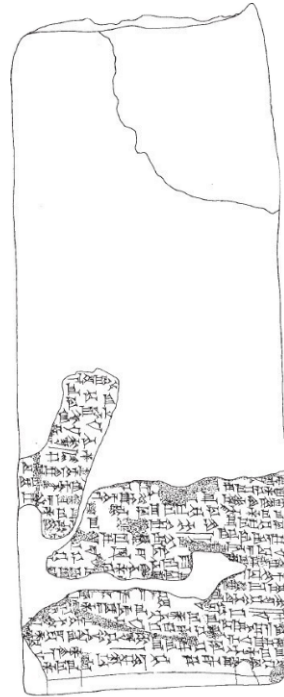
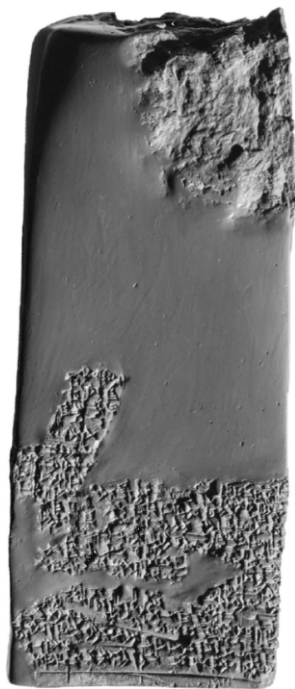


Figure 2 – Estimate of lactase production in adults worldwide.





Gallery 1.2 – Model contract for wool trade, side 2 of the Babylonian Prism, 25.5x9.5x9.5 cm, private collection.

On the other hand, wool was not widely used in Egypt since it was considered an impure material. With the spread of Islamism, however, this fibre was highly re-evaluated. In Denmark some woollen garments have been found, including a woman’s skirt and a belt, dating back to the third millennium BC, while some woollen fragments going back to 1000 BC come from the Hallstatt mines in Austria. The latter are olive green and have a plaid-like pattern with dark stripes.

As for ancient Greece, wool was mostly employed in the clothing sector, before more valuable textiles such as cotton and silk were introduced during the Hellenistic period. In the ruins of the city of Troy, for example, 8000 spindles have been found, while there are many iconographic works showing the complex and thorough procedure the Ancient Greeks used to work wool. The most famous pieces are certainly the Amasis Painter’s “lékhythos” (Figure 1.1), showing the different stages of weaving, and the mosaic found in the “House of Theseus” in Cyprus (Figure 1.2).



Figure 1.1 - Amasis Painter, black-figure attic Lekythos showing a group of women weaving wool, 6th century BC, Metropolitan Museum of Art





Figure 1.2 - "House of Theseus", detail from the "first bath of Achilles" mosaic, South wing, Cyprus, Nea Paphos Archaeological Park. From left to right, Peleus and Thetis, Achilles' parents, and the three fates Clotho, Lachesis and Atropos. Clotho is holding a spindle and a twisting bobbin for spinning

Processing wool was a woman's job (Figure 1.3 and Figure 1.4), and it was up to Greek women to evaluate the best technique to use in weaving, either the S or Z yarn twist, according to the function of the final product. The former consisted of spinning towards the left (clockwise) of the spindle, the latter in the opposite direction (anticlockwise). In order to make the fabric more dense and compact, the pieces underwent the process of fulling, which meant men stomped on them in a pit. In order to condition textiles, a specific clayey mud was used as a softener, while substances like urine and sodium bicarbonate were added if the fabrics had to be rough and stiff. Further post-treatment manufacturing operations included teaselling with teasels and brushes or bleaching white textiles using sulphur.



Figure 1.3 – Diosphos Painter, Gynaceum scene, 6th century BC, detail from an Attic black-figure Epinètron, 13.8 cmx31.5 cm, Paris, Louvre Museum.





Figure 1.4 – Triptolemos Painter, *Woman spinner*, 480-470 BC, Attic red-figure lekythos, Palermo, Museo archeologico regionale "Antonio Salinas".

The Greeks soon realized that a thorough selection of sheep was needed to drastically improve their textile fibres and the Romans continued on the same path. The finding of various samples of Anatolian wool supports the hypothesis that valuable fleeces were imported during the Roman times, especially from Miletos, Attica, Megara and Taranto, to produce more sophisticated fabrics. Since the Romans were in the constant pursuit of refinement for the fabrics they used to manufacture clothes, goat hair was not used in the clothing industry. On the other hand, it was a success in the production of coarse cloth, cloaks, carpets and slippers (Figure 1.5).



Figure 1.5 – Egyptian fragment of a clockwise swastika, roman or byzantine period, Paris, Louvre Museum.

Romans also introduced shears in the manufacturing of woollen products for the first time. This meant that the raw material was no longer directly pulled out of the sheep. The tool was made up of two sharp, curved blades fixed on a U-shaped spring. Together with brushes made of porcupine quills and metal combs, shears were widely used in *Officinae Lanificariae*, where the washing and willowing of textile fibre took place. After being washed and dried, wool went through the process of carding to make it homogeneous. This was needed for the before twisting and the spinning. It is important to highlight that, thanks to this process, lanoline was also obtained. This by-product is “wool fat”, a yellowish-white ointment that, at the time, was used for personal grooming: since it is easily absorbed by human skin, it was added to olive oil, almond oil and cocoa butter to produce creams.

During the Republican period *Textrinae* started to appear in the empire, closely connected to *Officinae Lanificariae*, since the demand for woollen clothing items started to grow significantly (Gallery 1.3).

“Woolen clothes were widely used, while linen, silk and cotton were exclusively for the rich. Dyed wool cost very little, from 2 to 4 as per pound (1 as=0.10 denarii, 1 denarius=4 sestertii).”

Based on the article “Moda e Abbigliamento nell’antica Roma” about the yarns and fabrics the Romans used for clothes, P. Virgili

“Spinning and weaving were mainly done by women, since it was considered an emblem of their virtues and dedication to their family. In Turia’s morgue, for example, the representation of a loom is enough to praise her virtues.”

Reported by the historian-philosopher Musonius Rufus, 1st century.

Gallery 1.3 – Documents.

Moreover some advanced techniques and tools were used in the cities of Pompeii, Herculaneum and Scafati. This led to the production of complex textiles, such as “*hybrid*” fabrics made of fibre of different kinds. During the archeological digs in Pompeii, 13 plants for willowing and carding wool, 5 for spinning and weaving and 3 *Officinae tinctoriae* were found. The finding of these facilities, together with that of terracotta jars and bowls with residues of dye, not only highlights the relevance and the remarkable development of this industry, but also lets us understand that the city was in a prominent position as regards the production of clothes. In Pompeii there are also ancient columns with images of some textile processes: the most famous one “*Fullones pillar*” (Gallery 1.4), is frescoed on three of the four sides. Another fascinating fresco can be found on the front of the “*Lanarii Coactiliarii*”, where the production of felt has been carefully illustrated. This particular type of



cloth was made by adding water, soap, glue and various animals' hair to the residues of other woollen fabrics and it was mainly used to manufacture heavy cloaks, head gear and footwear.



The man on the left is busy brushing wool cloth. The man on the right, standing beneath a caged dome, is engaged in fabric whitening via sulphurized fumigation. An owl is perched on top of the cage, which is symbolic of Athena, protector of the "lanaiuoli" (wool merchants).



Female workers hanging out some fabric.



Pressing machine for cloth.

Gallery 1.4 - Detail from the pylon from the Fullonica of Veranius Hypaseus, fresco, Naples, Museo Archeologico Nazionale

During the Roman Empire the first guilds of "lanarii" started to appear. These dealt with both the manufacturing and the trading of woollen items and were based in northern Italy, Pompeii, Tiatira and Epheous. These early facilities were essential for the future development of the clothing industry.

In medieval times, the economy was mainly founded on agriculture and sheep and goat farming, which were the main sources of the most consumed food and products, such as milk, meat and wool. Moreover, during that period, some types of wool were first differentiated, with the consequent distinction between simple and sophisticated woollen textiles. The most popular ones came from England, Saxony, Silesia, Italy and from the French city of Brie.

In the Early Middle Ages, the wool Industry spread throughout Europe with the Flanders as the main diffusion centre: in fact, this region exported a number of fabrics which were precious not only because of the fibre type, but also because of the dyeing process. The Flanders certainly promoted a trade internationalization: Flemish merchants purchased row materials in England, pressed them in their country of origin, and sold the final product to French and Italian people. The great fairs contributed to the expansion of commercial exchanges, presenting the row materials as



well as offering a large variety of working machines and colouring matters. Italy, after going through a period of serious crisis following barbarian invasions, started recovering, thanks to the possibility of trading with Spain, France, England and Middle Eastern countries; consequently, important productive sites were born in the northern area.



Figure 1.6 - Tile of the Florence's Cathedral, Andrea Pisano, 14th century.

During the Late Middle Age, we witnessed the development of guilds, associations of workers belonging to the same productive sector protecting artisans and merchants. In this period Tuscan wool merchants were able to increase the importance of their wools on the market making them sought after throughout Europe. The representation of the weaving process on a tile on the bell tower of Florence's Cathedral (Figure 1.6) shows the leading position of this activity in the Florentine society.

At the same time, in Orvieto, a miniature (Figure 1.7) shows the main guilds of that area, including the woollen guild, the weavers' guild, the flax dressers' guild and the dyers' guild. Moreover, in Bologna a depiction of Porta Ravegnana's Market shows a large amount of fabrics, hand-tailored clothes, tanned skins and headgears.

This occurrence spread to all the most important cities (Genoa, Lucca, Perugia, Naples) up to Veneto and Lombardy, widely active especially in the 15th century: in Venice, the woollen guild called "*la Mariegola dei Lanieri*", which was added to the sixteen most important guilds allowed to participate in the Duke's election, competed strongly on the Florentine markets. In Italy the textile industry thus became one of the main sources of income and the woollen guild acquired prestige and importance even politically, as demonstrated by the magnificence of its premises like those in Florence.



Figure 1.7 – Orvieto's miniature representing arts and jobs



In the following centuries England, France and Flanders became important centres of wool processing: in England, in particular, in 1370 the production was already well-developed and varied, with 44 different types of wool. Societies called "Merchants of the Staple" (Figure 1.8), coordinating the commercial transactions of the woollen sector were formed, and, during the reign of king Edward III (1312-1377), the first "Staple" cities, purchasing and exporting wool and final products, were formed. In the meantime, England encouraged weavers', dyers' and experts' immigration, welcomed refugees from other countries escaping from their homeland because of wars or persecutions and the government introduced laws forbidding the exportation of sheep and unprocessed wool. Thanks to these policies, England became very competitive on the markets, so much so that Henry VIII's reign reached its splendour thanks to the development of the woollen sector, and started producing sophisticated fabrics, that smoked the competition of the Flanders on the market: for the first time wool fibres were weaved together with linen fibres and new dyeing and finishing techniques were invented. The trade flows became really active with continental Europe: in Bologna English fabrics importation was so massive that the guild called "*Mercatores Drapariae Angliae*" was formed.

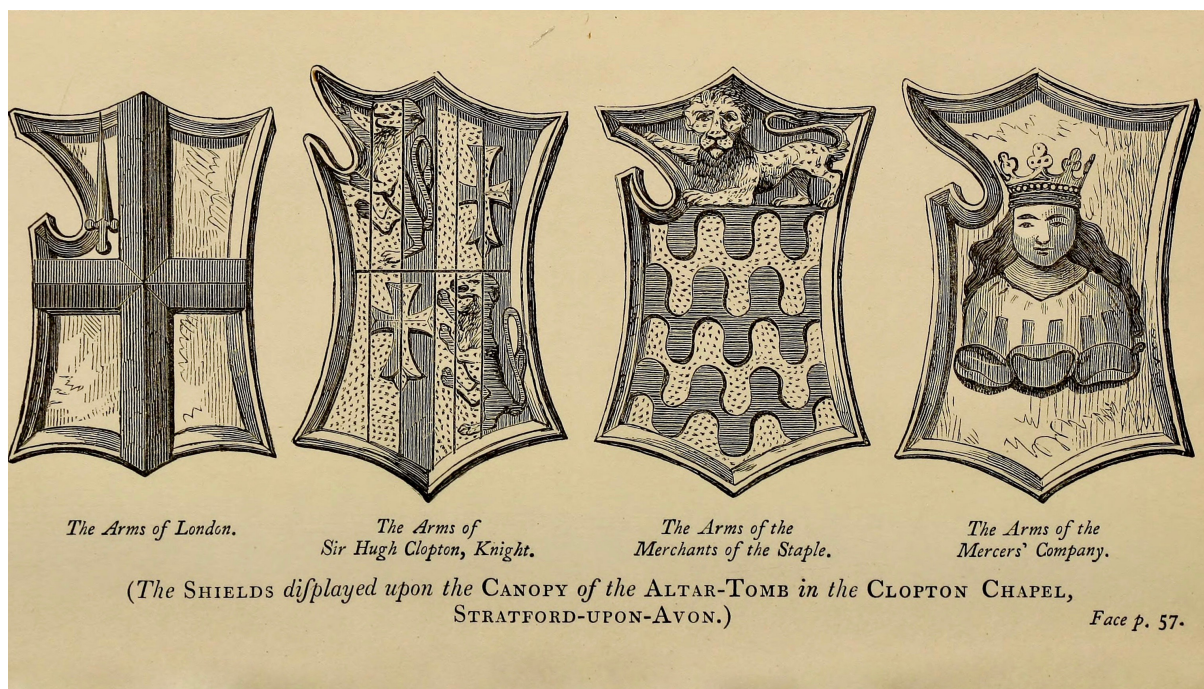


Figure 1.8 – Bellew, J. C. M., “Shakespeare's Home at New Place, Stratford-upon-Avon”, London, Virtue brothers and co., 1863. The third crest represents the “Merchants of The Staple”.

In Spain, between 1400 and 1700, the fine wool of merino sheep distinguished itself: it was a breed originating in Northern Africa, crossed and selected by Castilian shepherds and closely guarded, avoiding its exportation for a long time. The flourishing trade of this variety of wool, in great demand in the Flanders, helped finance Colombo's journeys in the 14th century. During the period of geographical explorations, the Conquistadores' work enabled sheep farming to spread further to countries a long way from Europe: firstly in Cuba and Santo Domingo, and later, after Cortés' journeys, even in the current Mexico and South-western United States.



The English tried to discourage the growing wool industry in Northern America, making the wool trade punishable by the "cut of the right hand" of the guilty; however this didn't prevent this sector from developing until the American Independence War (1775-1783) partly thanks to the policy promoted by the presidents George Washington and Thomas Jefferson. The technological innovation that determined the flourishing development of the American wool sector was the spinning wheel called "Spinning Jenny" (Figure 1.9), patented in 1764 by Thomas Hights on the peak of the Industrial Revolution. This machinery was equipped with a hand-crank wheel, able to trigger the rotation of eight wooden spindles, thus causing the yarn twist and its concentration around one spindle: in this way only one worker could spin several yarns at the same time. With the previous hand looms this process was far slower. This enabled a strong decrease in the labour, which turned out to be a great advantage for American industries.

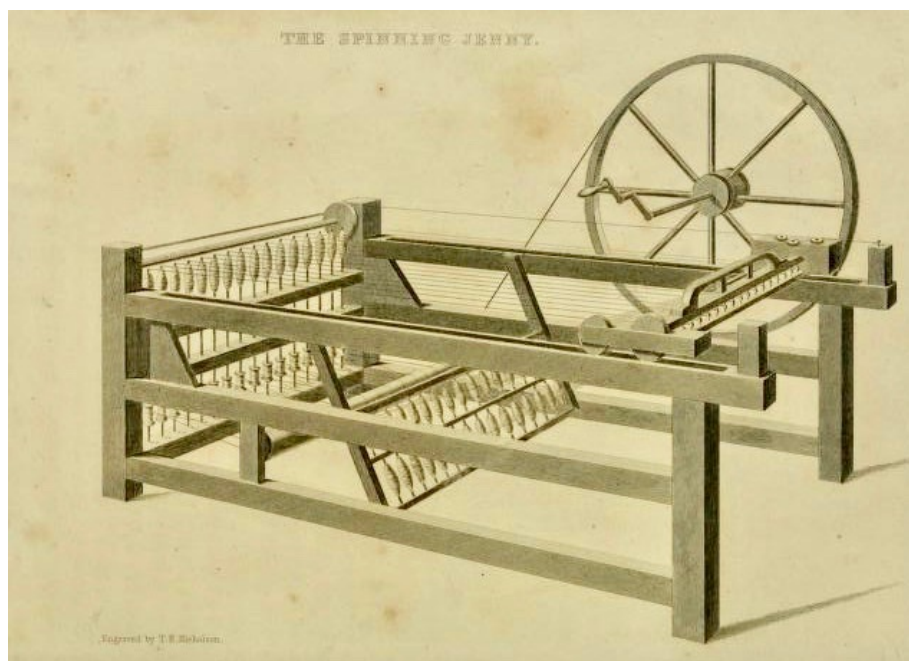


Figure 1.9 – The spinning wheel Spinning Jenny, invented by James Hargreaves in 1764.

This first revolutionary invention was followed in England by the "water frame" hydraulic spinning (Figure 1.10) wheel designed by Richard Arkwright in 1769. This new machinery was an important watershed for the making of warp yarns, by replacing human fingers with wooden and metal cylinder, thus enabling the production of cheap fabrics starting from cheap yarns. This laid the foundations for the success of the cotton industry. In 1784 Edmund Cartwright patented the first power loom: an invention that enabled the production of smooth cloth at a speed ten times greater than handlooms.



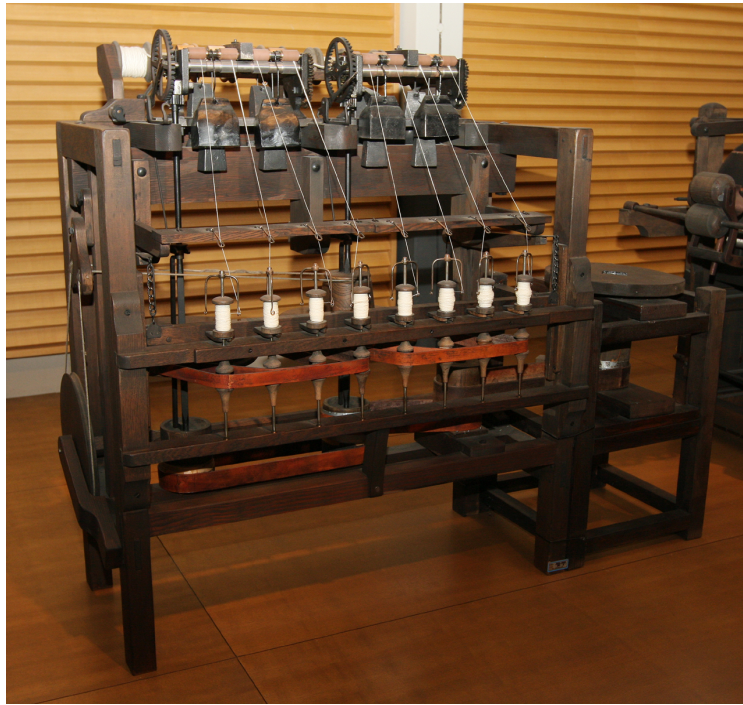


Figure 1.10 – The hydraulic spinning wheel water-frame. invented in 1769 by Richard Arkwright.

In the first half of the 19th century the processing methods, increasingly standardized and needing less labour led to forms of violent uprisings, in particular Luddism, a protest movement where the workers sabotaged industrial machinery. France and Belgium, had experienced something similar in the 14th century because of the introduction of the fulling mill, a machinery for waterproofing wool. After being repressed, with the fall of the Napoleonic Empire and the diffusion of new political ideas, Luddism gradually lost strength and disappeared completely around the 1830s.

Nowadays the wool sector is mainly developed in non-European countries such as China and Turkey. Italy stands out as the major European producer and the world's second largest exporter after Chinese juggernaut. However, wool clothes' production is now falling, mainly because of synthetic fibres, like polyester, easily washable and cheaper.



2 – CHARACTERISTICS

1. Chemical composition

Wool contains 85% of keratin, a protein that contains sulphur (Figure 2.1), 12% proteins that do not contain sulphur, 1-2% lipid substances and a small amount of mineral salts.

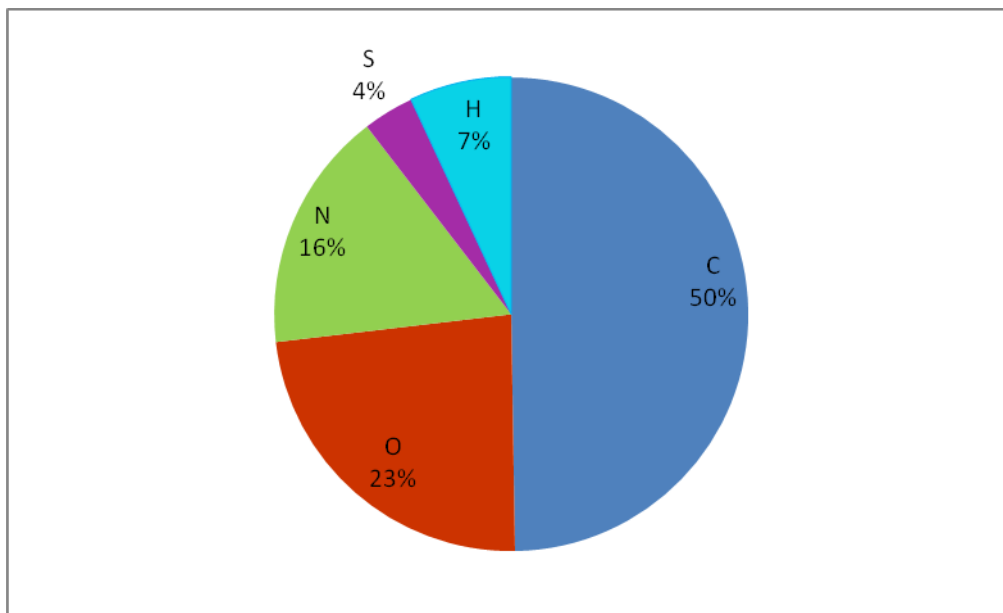


Figure 2.1 – Concentration % of H, S, C, N, O inside keratin.

All the different types of wool contain proteins that differ because of their nature and the quantity of amino-acids inside them; the table below shows the composition of amino-acids inside merino wool, referred to the hydrolyzed product and expressed in moles%.

<i>Glutamic acid</i>	<i>15,22</i>	<i>Aspartic acid</i>	<i>7,19</i>
<i>Cystine</i>	<i>11,34</i>	<i>Tryptophane</i>	<i>6,39</i>
<i>Cysteine</i>	<i>0,14</i>	<i>Tyrosine</i>	<i>6,34</i>
<i>Cystine SO₃H</i>	<i>0,60</i>	<i>Valine</i>	<i>5,62</i>
<i>Serine</i>	<i>10,79</i>	<i>Glycine</i>	<i>5,59</i>
<i>Arginine</i>	<i>9,79</i>	<i>Alanine</i>	<i>4,58</i>
<i>Leucine</i>	<i>9,06</i>	<i>Lysine</i>	<i>3,92</i>
<i>Isoleucine</i>	<i>3,20</i>	<i>Phenylalanine</i>	<i>3,51</i>
<i>Proline</i>	<i>7,93</i>	<i>Histidine</i>	<i>1,07</i>

Table 2.1 – Composition of amino-acids inside the merino wool, referred to the hydrolyzed product and expressed in moles%.



Each amino-acid has a key role in determining the protein structure and operation; for example, the cysteine, thanks to his functional group –SH, can make, with other molecules, intramolecular disulfide bridges (S-S), which contributes to the stabilization of the tertiary structure.

Wool's lipids contain 40 % sterol (e.g. cholesterol), 30 % polar lipids (e.g. sphingolipids) and 25 % fatty acids.

Impurities

Raw wool has a percentage of foreign material that varies from 15 % to 72 %. Fibers are in fact assembled in greasy and waxy locks, which make it difficult to separate them; they come from the secretion of sebaceous and sweat glands, and from keratin's degradation. The fleece also contains other substances such as sand, earth, grass etc., gathered during the pasture.

These substances can be divided into two main groups: *suint* (soluble in water) and *suinthin* (insoluble in water). The former is made up of potassium salts of fatty acids, phosphates, sulphates, potassium chloride, calcium, ammonium, urea and its derivatives. The latter, also known as *wool's fat*, *wax* or *lanoline*, despite its insolubility, can be emulsified through the use of surfactants. Lanoline is extracted from the fleece, and treated with alkaline solutions and surfactants; the emulsion is then centrifuged or broken down, by lowering the pH from 10.5 to 3, and subsequently purified. In its chemical composition there are some esters of fatty acids and free fatty acids, such as the palmitic one, and, in smaller quantities, oleic, stearic and butyric acids. This “waste” substance, thanks to its soothing, absorbent, disinfectant and softening properties, is widely used in the leather, cosmetic and also pharmaceutical industry (Figure 2.2).

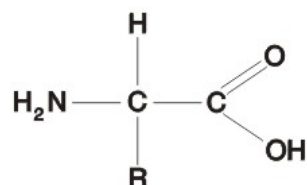


Figure 2.2 – Lanoline mixture usable for the production of creams and cosmetics.

Detailed study

Amino-acids

Amino-acids are the monomers that constitute proteins. They are organic compounds, whose name is due to the presence in their structure of an acid functional group (carboxylic group, $-\text{COOH}$) and a basic ammonic group ($-\text{NH}_2$).



Depending on the R radical's nature, amino-acids can be polar or not (Figure 1).

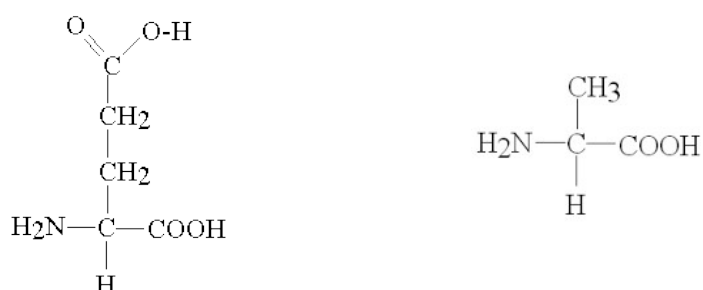


Figure 1 – Glutamic acid (left) and alanine (right) respectively are examples of polar and non-polar amino-acids.

Inside proteins, amino-acids bind thanks to the reaction between the carboxylic group of an amino-acid and the ammonic group, thus forming the creation of a peptide bond (Figure 2). During the reaction, called polycondensation, one water molecule for each bond formed is eliminated.

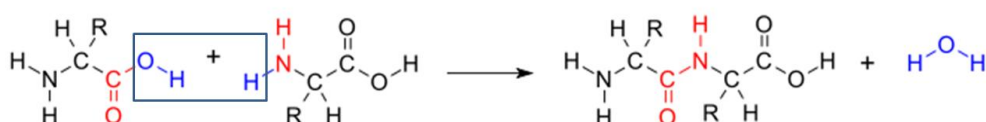


Figure 2 - Formation of the peptide bond.



2. Classification of textile fibres

Textile fibres are classified as natural or man-made, depending on their origin.

Natural fibres are found in nature as longer or shorter fibres and, as shown in Figure 2.1, they may originate from animals or plants; examples of natural fibres are wool or silk.

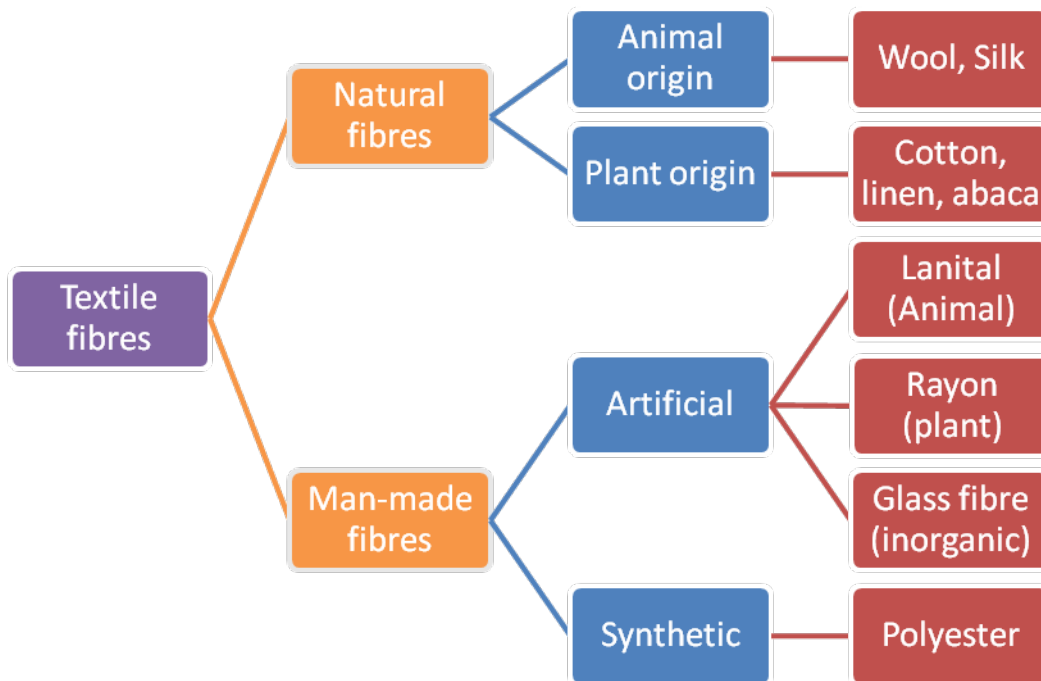


Figure 2.3 - Classification of textile fibres: an outline

Man-made fibres can be artificial or synthetic. Artificial fibres are made of natural polymers: e.g. lanital, rayon and glass fibre. Synthetic fibres are made of synthetic polymers, which are large molecules, macromolecules, created by men. Polyester (Figure 2.4) is a man-made synthetic fibre.



Figure 2.4 - Polyester fibre

From the very beginning of the last century, natural fibres have had no rivals. In fact, it was only in the first years of the 20th century that man-made fibres began to be discovered. For example, viscose, or artificial silk was discovered in 1883 and produced in factories in 1906. The new fibres had several advantages such as: the price, the resistance and the water-resistance. But, at the same time, those new discoveries had some disadvantages: for example, viscose is highly flammable. Many of those problems were solved with successive discoveries. However, still today many



man-made fibres, particularly those made with derivatives of oil, are flammable or get easily ruined by high temperature washings.

Textile fibres are mainly made of organic macromolecules.

Natural fibres of animal origin are mainly made of keratin, the protein which makes up human and animal hair. However in the case of the animals that secrete fibres utilised in the textile industry the protein that mainly makes up the fibre is the fibroin.

Natural fibres that originate from plants are made of cellulose, a polysaccharide made up of glucose molecules ($C_6H_{12}O_6$).

Artificial fibres of animal origin come from animal proteins such as the casein of the milk, in the case of lanital; artificial fibres having a plant origin are made up of a protein extracted from plant seeds or of laboratory-treated cellulose. Inorganic artificial fibres of mineral origin are glass fibre made up of silica added to sodium carbonate or to boric acid and borax, and metallic fibres.

Synthetic fibres are classified depending on the family to which the constitutive polymers belong: polyolefinic, polyacrylic, polyamidic, polyesters, polyurethanic and elastomeric obtained from synthetic rubber.

Detailed study

The polymers

Polymers are also called macromolecules because of their high molecular weight. They are long chains of monomers (Figure 2.3), bounded together by the same type of bond as shown in Figure 2, the covalent bond.



Figure 1 – The repetitive units, the monomers.

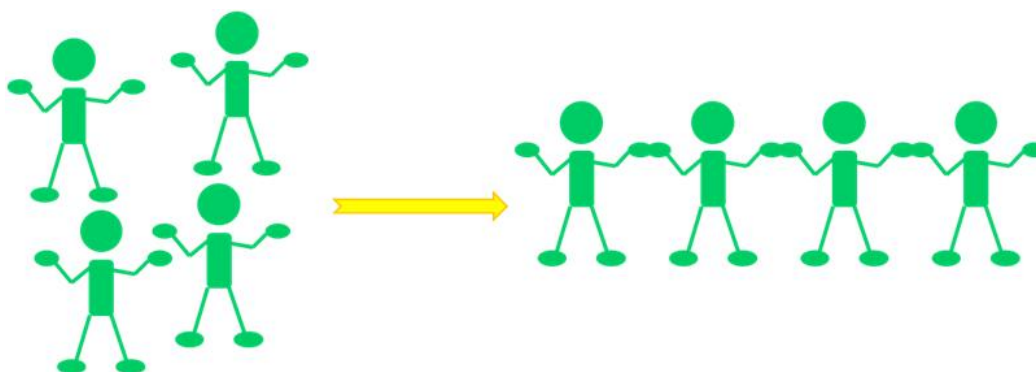
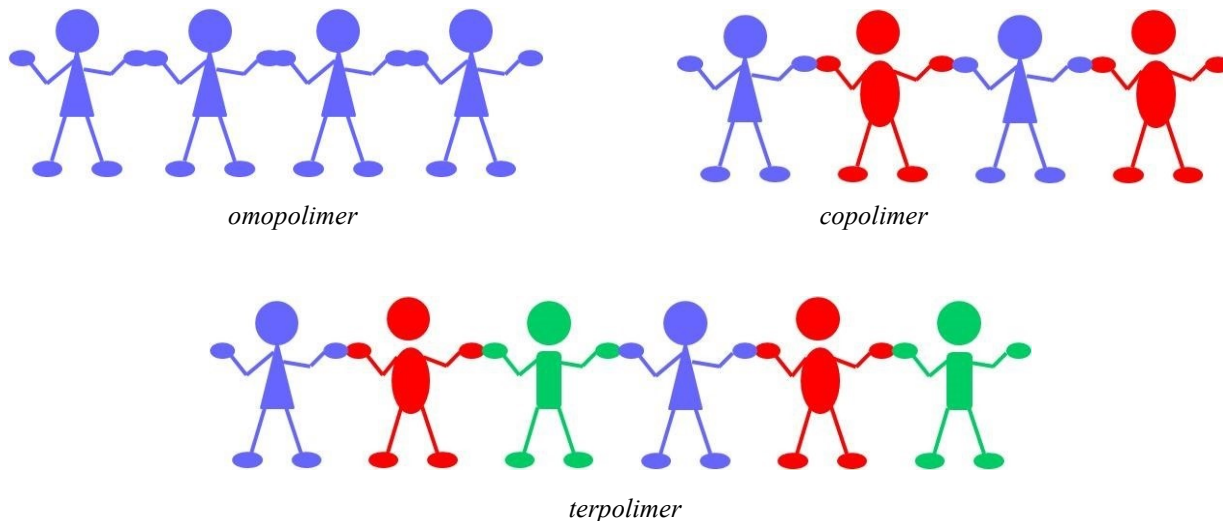


Figure 2 – polymerization.



Polymers may also be classified based on which monomers make them up: if the monomers are all the same the polymer is called homopolymer; if, they are made up of two different monomers it is called copolymer; if three, terpolymer and so on.



Polymers found in nature are defined polymers of natural origin, those recreated or laboratory-modified from polymers which can be found in nature are called artificial polymers. Synthetic polymers are polymers laboratory-created with man-made monomers; an example is Polyvinyl chloride (PVC) which is made up of the monomer $\text{CH}_2=\text{CH}-\text{Cl}$ (Figure 2.6).

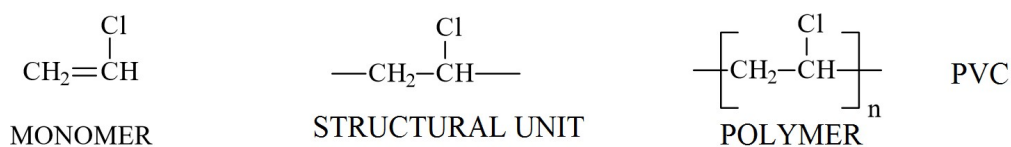


Figure 3 – II PVC.



3. Keratins

Keratins are a family of fibrous proteins, insoluble in water and in solutions slightly acidic or basic, resistant to proteases, which are present on the coverings of all terrestrial vertebrates; they are produced by epidermal cells called keratinocytes, in whose cytoplasm they are immersed in the form of intermediate filaments.

Its chemical composition has a high content of a sulphur amino acid (in the amount of almost 3 %), cysteine (Figure 2.5), responsible for the characteristic smell, following a combustion, and which influences the rigidity of the protein.

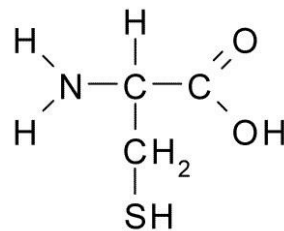


Figure 2.5 - Cysteine molecule

The keratin can be found in two morphologically different forms, depending on its secondary structure, which can be α -helix or β -pleated sheet: we therefore have α -keratin, present in mammals, and β -keratin, in birds and reptiles (Figure 2.6). In wool, only α -keratins are present, which are transformed into β -keratins, if the fibre is subjected to a tension.

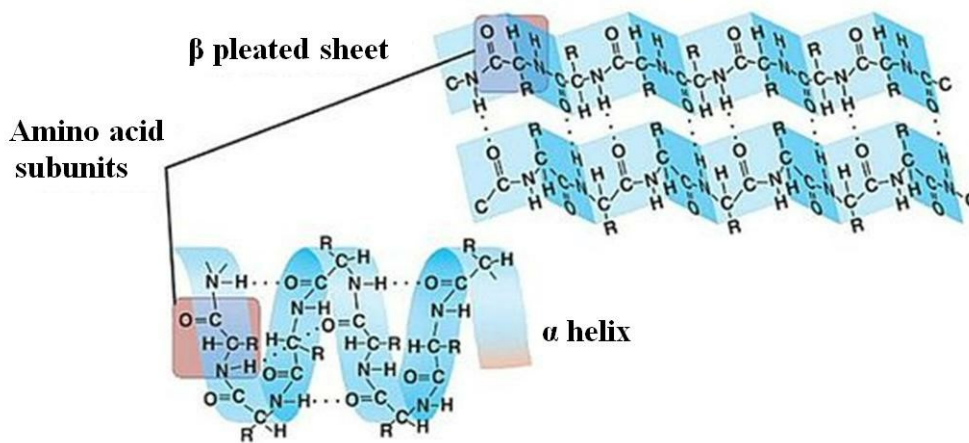


Figure 2.6 - α -helix and β -pleated sheet structures

The type of structure depends on the amino-acidic composition and, consequently, on the type of chemical bonds which are established between the lateral chains: interchain interactions can occur, which involve residues of amino acids belonging to different polypeptide chains and which facilitate the formation of crystalline zones, or intrachain interactions can occur, established between R groups arranged on the chain itself (Figure 2.7), which tend to create amorphous zones.



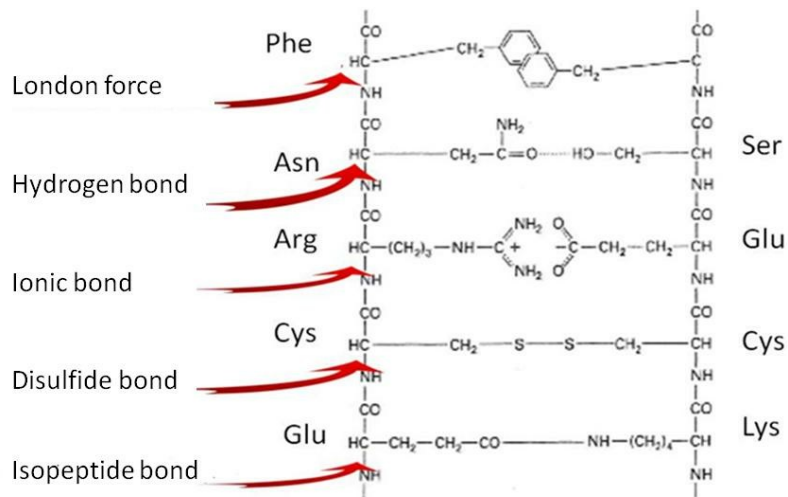


Figure 2.7 - Examples of bonds occurring between R groups of a polypeptide chain

In particular, there are:

- saline bridges: ionic bonds between groups of opposite charge, generally between -NH_3^+ and -COO^- ;
- disulfide bridges: real covalent bonds, formed between two -SH groups belonging to two different residues of cysteine;
- hydrogen bridges: atoms of hydrogen are involved, with a partial positive charge (δ^+) because they are covalently bonded with highly electronegative elements (fluorine (F), oxygen (O), nitrogen (N)), which are attracted by close electronegative atoms.

Wool's proteins are all α -keratins, which are classified according to their composition in amino acids:

Protein fraction	% mass	Number of amino acids	% in mass of sulphur	Characteristic
Low content in sulphur	58	392 - 416	1,5 - 2	< 16 % mol cysteine
High content in sulphur	18	94 - 211	4 - 6	16 - 24% mol cysteine
Ultra-high content in sulphur	8	168 - 197	8	33- 37% mol cysteine
High content in glycine and tyrosine	6	61 - 84	0,5 - 2	16 - 24% mol glycine and tyrosine

The organisation of an α -keratin is rather complex, and it is called "*coiled-coil structure*": a shape characterised by several woven α -helix chains and stabilised by hydrophobic interactions between the non-polar residues along the helix (Figure 2.8).



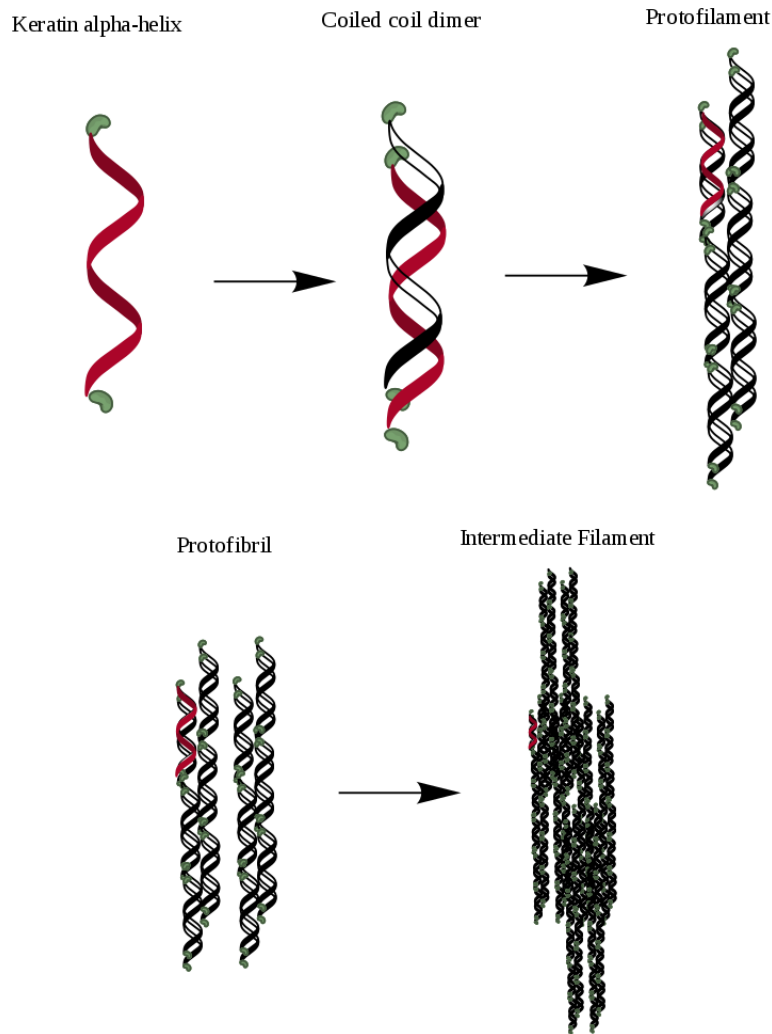


Figure 2.8- Structure of an α -keratin

Two right-handed α -helixes wrap themselves and form a dimer which, through an end-to-end connection, ties with another dimer to form some protofilaments. These, arranging themselves in a circle, produce a protofibril: the bond with disulfide bridges of four protofibrils allows the creation of a microfibril. Each microfibril follows the “9+2” pattern which consists of the union of 11 protofilaments or protofibrils, nine organised in a circle and two in the centre. Besides, the α -keratin is able to create transversal bonds between adjacent polypeptide chains, for example through disulphide bridges or isopeptide bonds between a carboxylic group ($-\text{COOH}$) and an amino group ($-\text{NH}_2$), situated laterally on the chain. It is precisely these bonds which influence the reactions of the wool's fibre when it is subjected to various treatments, such as, for example, heating in boiling water.



4. Physical characteristics of wool

In this chapter the main characteristics of wool are described. These properties are not constant but are influenced by environmental conditions such as temperature and humidity. Wool fibres have a curl that tends to take a helical shape with more undulations in the finer types. This structure gives elasticity and cohesion to the fibres, it improves wear resistance, bulkiness, thermal insulation and resilience. Moist heat, since it reduces the curl it diminishes these qualities.

Table 2.2 shows the values of the main physical properties of wool.

Property	Value
Specific weight	1,31 – 1,32 (g/cm ³)
Toughness – dry	10,5 – 14,6 (cN/tex)
Toughness – moist	6,1 – 14,1 (cN/tex)
Thermal conductivity	0,03 (W/mK)
Stretching at break	35 – 25 %
Temperature of combustion	205 °C
Specific heat	0,325-0,326 (Kcal/Kg °C)
L.O.I. (Limiting Oxygen Index)	25 %

Table 2.2 – Main physical parameters of wool fibres

Toughness

Toughness is the breaking strength of the fibre. Generally it is expressed in cN/dtex (cN is the abbreviation for centinewton, so it corresponds to 0.01 Newton; tex is a linear density value, a mass measurement per length unit, which corresponds to a gram per kilometre). Toughness values state the behaviour of the material at the extreme limit of stress. Wool's toughness values are not very high, they are usually lower than the values of the other natural fibres (cotton, flax, silk) and synthetic fibres (nylon, acrylic, polyester).

Elasticity

Elasticity is the property that allows the fibre to stretch when subjected to tension. Wool fibres in comparison with other textile fibres have more extensibility, a minor strain at break, this means that it takes less stress to cause the breakage of the fibre, and a higher elasticity when they are humid or wet thus showing an attitude similar to hair. This behaviour is clearly shown by the stress-strain curves of the graph in Figure 2.9 which have been obtained by putting the wool fibres in an environment with a specific value of relative humidity, indicated next to each curve, and at constant temperature.



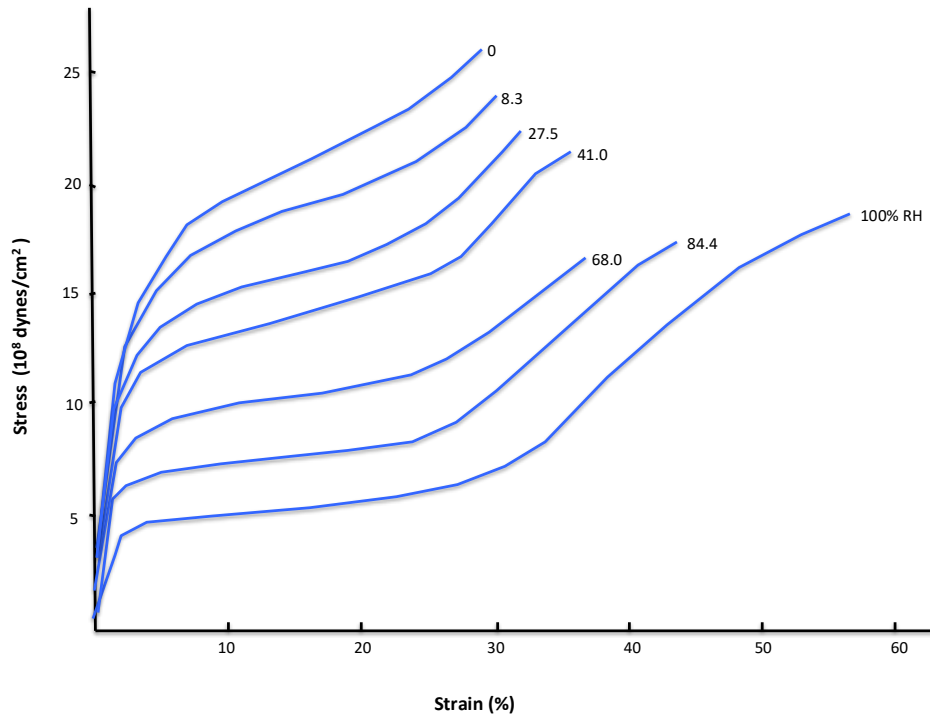


Figure 2.9 – Stress-strain graph of some wool fibres with different contents of water (the dyne is a unit of measurement that belongs to the CGS system and indicates the force and it corresponds to 10^{-5} N), (from Hearle, Chapman, Senior 1971, adapted)

Flexibility

Wool has a high flexibility. A wool fibre can be folded on itself more than 20 000 times without breaking, in contrast with the 3,000 times for cotton and 2,000 times for silk.

Resilience

Resilience is the capacity to absorb mechanical work without suffering permanent deformations. Wool, due to its polypeptide chains, acts as a spring: it expands when subjected to traction and retracts when the traction stops. For example a wool textile, when it is subjected to a deforming action, although slowly, it returns to its initial form. It can extend for up to 50% of its original length when it is wet and up to 30% when it is dry, but it will return to its original dimension when the tension stops. The return to initial conditions is accelerated by humidity.

Felting property

It is the union of the fibres together due to the combined action of rubbing, heat and humidity. It is due to the fact that the fibres are arranged like tiles on a roof in the same direction and towards the tip of the fibre; in that way the fibres are able to move freely between them in one direction but in the other are hindered, the result being a lifting of the fibres that facilitates wool's tangling.

Hygroscopic nature

Due to this property wool is capable to absorb humidity up to 30% of its weight without suffering from alterations or changes in shape. Water molecules, small, mobile and polar are able to penetrate fibres, to interact with hydrophilic amino acids and to form hydrogen bonds with some residues like the carbonyl or hydroxyl. This allows the fibre to attract and incorporate water molecules in the



structure, contrary to what happens in the sponge where the absorption is capillary. Therefore in case of a humid climate or intense sweating, wool absorbs the humidity and releases it slowly to the surrounding environment avoiding a sudden cooling of the body.

Thermal insulation

It is thermal insulation capacity (cold and hot). The capacity of insulation of textile fibres depends on the amount of air that they are able to trap: the insulating power increases with the increase of amount of air trapped. Wool flakes give roughness to the fibre and they increase the surface. Thanks to these characteristics wool fibres are able to store and to hold a greater amount of air. Different types of wool have different insulation values and usually finer wool has greater insulation values (Merino wool). The λ coefficient of thermal conductivity of sheep wool is 0.03 W/mK, which gives it a thermal insulation capacity, constant even in the presence of moisture, higher than any other natural material. Wool's specific heat is 0.325-0.326 Kcal/Kg°C.

Combustion

Wool is a textile partially fireproof thanks to the humidity trapped by its fibres. In fact the limiting oxygen index (L.O.I.), that is the value which indicates the minimum quantity of oxygen necessary for the fibre to burn, is 25%, which is higher than the percentage of oxygen in the air, for this reason wool rarely bursts into flames. In addition through wool fibres the flame does not spread, it produces little heat and smoke and it does not melt thus avoiding serious burns from incandescent material. If it burns it releases in the air carbon dioxide and sulphur molecules because of the breakage of disulphide bonds.

Resistance

Wool has the ability to resist acids while it is very sensitive, especially when hot, to alkaline agents. Its helical structure increases the wear resistance whereas its chemical composition makes wool resistant to the attacks from mould and bacteria, however it is not resistant to moths.

Yellowing

Wool fibres tend to turn yellow when subjected to sunlight and they become weak because of heat. A long exposure of wool fibres to UV radiations ($\lambda < 380$ nm) leads, with processes of photo-oxidation and photochemical deterioration, to a yellowing and a decay of their mechanical characteristics with consequent embrittlement. The process is therefore composed of different phases, shown in figure 2.10, whose speed varies depending on the humidity conditions; indeed the speed of yellowing is less high in condition of dryness.



Figure 2.9 – Phases of the yellowing of wool

Electrical properties

When wool is dry it is not able to conduct electricity, whereas if it is moist it becomes a conductor.





5. Morphological structure of wool fiber

Wool fiber is made up of an outer part called cuticle, which consists of three layers; the first one is the *epicuticle*, which is a hydrophobic membrane that protects the fibre. This layer is the only non-protein part made of waterproof waxy material, and has got tiny holes so that steam or other small molecules may pass through. Under the epicuticle there is a second layer called *exocuticle*, made up of flakes, all of which point at the same direction as the fibre. The innermost layer is the *endocuticle*, which is the only one that tends to inflate when touching water.

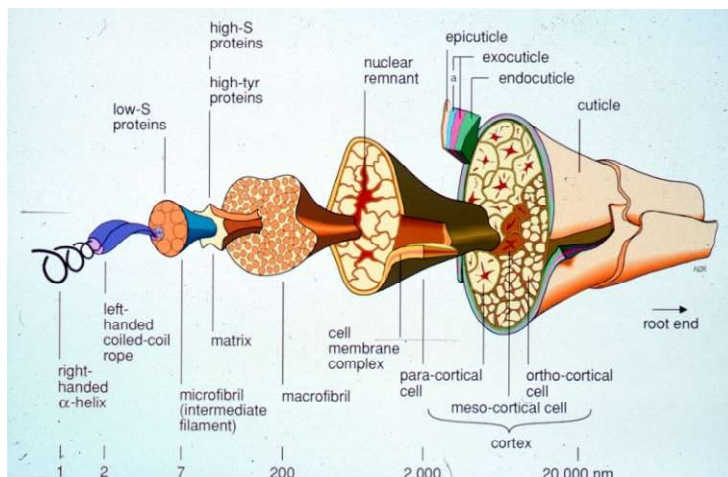


Figure 2.11 - Structure of a wool fiber

This arrangement (Figure 2.11) is crucial for some of wool's features, such as the felting power. As a matter of fact, when in an alkaline solution (water and soap) and with hot water, wool felts rather quickly: the tiny flakes open up in the water and bump into the other fibers' scales; due to the movement and the pressure, fibers dovetail in a solid and resistant structure.

Wool shrinks when felting: its shrinking percentage varies between 30 and 50% of its original size and depends on its quality, thickness used and on the making time.

Under the cuticle there is the *cortex*, made up of fusiform keratinized cells containing microfibril bundle with alpha-helix structure twisted together. In the middle of less fine wools there is a cavity called marrow, which has cellular residues inside, these wools are, these wools are more difficult to spin and to dye.

The cortex is divided into two parts: the *ortocortex* and the *paracortex*, with extremely different characteristics one from another. In fact, in the ortocortex there are the shorter and wider cells with no nuclear residues, more reactive and, in basic state, tend to colour more intensely and to dilate more than the paracortex cells. This big difference is due to the presence of intralocked bridges in the ortocortex (inside the same chain) which don't let them arrange in a neat way, while thanks to interlocked bridges (between one chain and another) which help the formation of more neat and solid areas, they become more difficult to attack by chemical reagents.



3 – UTILIZATIONS

1. Wool production

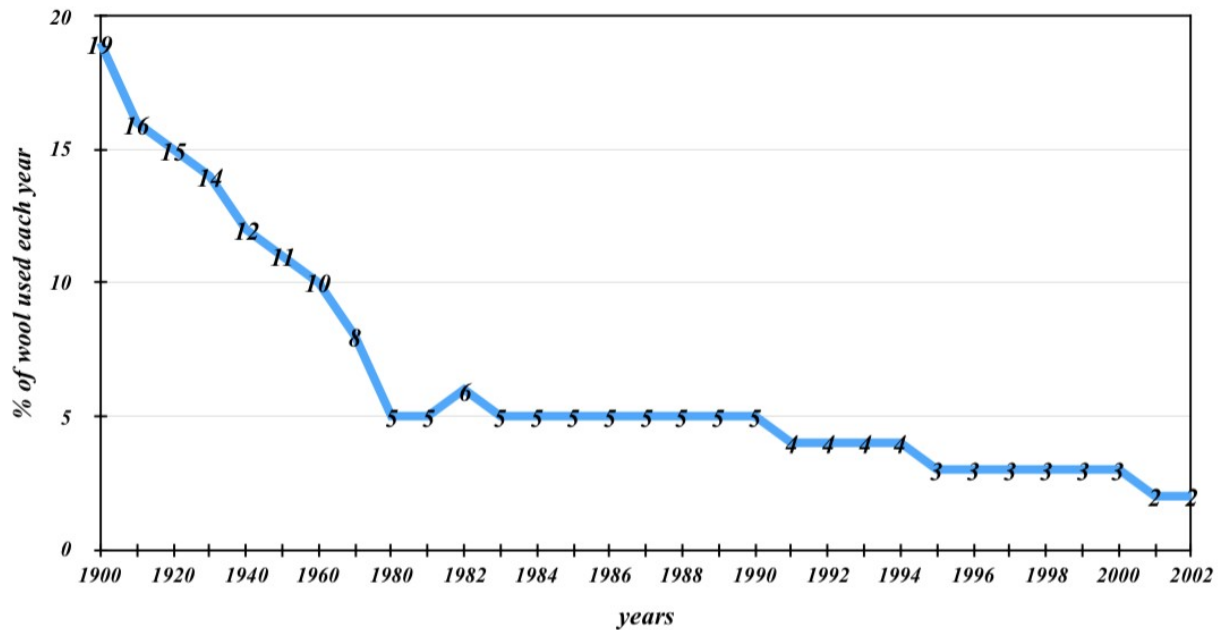


Figure 3.1 - The graph shows the percentage of wool used in the textile industry between 1900 and 2002.

Wool is the main sheep product. Nevertheless in the few last decades it is been going through a period of strong crisis because of the competition in the textile sector, the most profitable market for this type of fibre. In fact in the early 1990s its production amounted to 3 million tons whereas now it does not exceed 2 million and 200 thousand tons. This drop has been caused by the increasing interest in synthetic fibres such as polyester, which are more used than natural fibres because of their low price. Nowadays the main producers of wool are Australia, New Zealand and China. Even though the first two have been affected by the increasing competition from China and India, which have invested heavily in sheep farming in the last few decades, they respectively account for 21 % and 10 % of the world's supply (Table 3.1).

Country	Production in 2007	Production in 1997
Australia	21.4 %	30.4%
China	18.2 %	10.6%
New Zealand	10.0%	11.4%
United Kingdom	2.9%	2.7%
Italy	0.4%	0.5%

Table 3.1 - Decrease in wool production between 1997 and 2007 in major producing countries.



In Europe, the main producer of wool is the United Kingdom. The British Wool Marketing Board, a non-profit making organization, coordinates and manages the wool trade on the domestic market as well as the international market.

As regards Italy, although in the past it had a crucial role for the production of high quality wool, now Italian wool looks less appealing. Due to its high productive cost and its productive shortage, wool is sold at 0.50 €/kg and the profit does not cover the cost of shearing and farming. As a consequence, nowadays in Italy, sheep are bred mainly for their meat and milk.

However, even though now wool is no longer used in the textile industry to produce high quality clothes, sheep still need to be sheared. It is estimated that every year in Europe 200 tons of wool are produced (10 % only in Italy) and their disposal is a serious problem.

In fact the European legislation about hygiene and health establishes that wool must be considered as hazardous waste because it can be dangerous or potentially harmful to human health. As a result it must be packed and taken to specific waste treatment plants with high environmental and economic costs for the producers because, when it is polluted with filth and humus, it can transmit diseases and infections. Therefore wool can no longer be disposed of as it was in the past when farmers left it on grazing land or burnt it thus releasing an enormous amount of toxic gases, such as carbon dioxide and sulphur.

To find a quick solution to the issue of waste disposal, in the last few years some researches have been carried out. Their aim is to find alternative and eco-friendly uses of wool. Some possible solutions have already been found, for example it can be put as an insulation board into roofs, as a gauze on wounds, as a fertilizer in agriculture or as a water purifier.



7. Agriculture

Thanks to the use of new technologies, raw wool or recycled wool today can also be used in the agricultural sector as a nitrogenous fertiliser; Although there are still few research institutes in Italy in this field, a project has already been launched in Italy that has led to excellent results in fertilisation through wool recycling: the Greenwolf project (Figure 3.2). The companies involved in the project are: ISMAC (Institute for the Study of Macromolecules) of belonging to CNR of Biella, the Polytechnic of Turin and the textile machinery company Obem Spa.

The project aims to obtain from wool wastes "hydrolysed wool", which can be used as a natural fertiliser that can increase the nitrogen and carbon content of the soil and its ability to retain water.

When the wool is treated with overheated water above about 180 degrees, a hydrolysis process of its proteins takes place, resulting in faster nitrogen release with fertilising action; what the researchers are trying to define are the right temperature, pressure and time parameters.



Figure 3.3 – The equipment used in the Greenwolf project.

To produce hydrolysed wool, a load of 6 to 20 kg of wool wastes is centrifuged at a speed of 12 revolutions per minute for about 30-90 minutes (depending on the amount of wool) at a constant temperature of 180°C, inside a plant quite similar, in appearance, to a concrete mixer (Figure 3.3).

This is a completely ecological treatment: because it does not entail the washing of wool with polluting and environmentally harmful solvents, it can be considered a process of "green hydrolysis" whose end products are hydrolysed proteins, characterised by low levels of amino acids and peptides with a low molecular weight.

Silvio Sicardi, full professor of chemical engineering principles at the Polytechnic of Turin, explains:

"There are no wastes. The water is completely vaporised and the hydrogen sulphide is neutralised and transformed into a sulphate that ends up in the fertilizer".

Based on the degree of hydrolysis, both the rate of release of nutrients and bio-stimulants and the ability to retain water can be adjusted, thus making the hydrolysed wool a good substitute for the fertilisers that have the same capabilities. Protein hydrolysates are permitted in agriculture and are particularly suitable for leaf fertilisation, thanks to their bio-stimulating properties. It is believed that the fertiliser obtained has both an immediate fertilising effect and a long-lasting nutritional ef-



Green hydrolysis conversion of Wool wastes into organic nitrogen Fertilisers

Figure 3.2 - The logo of the Greenwolf project



fect (up to 5 months), thereby providing the plant with the nutrients it needs for the whole season with only one fertiliser. Thanks to the good hygroscopic ability of sheep's wool, the fertiliser could also help to retain more water, thereby allowing plants to better cope with droughts. The characteristics of the fertiliser obtained from the process could emulate, then, those of soil improvers, acting on the ground with the same effectiveness and the same advantages.

The benefits of the project are both environmental and economic:

- Environmental: by recycling 100% of the wool, this will no longer accumulate in dumps, but will be used to fertilise productive and profitable lands such as gardens, pastures, fields and orchards. In addition, the ability to retain leachate waters could be enhanced, by retaining its hydrophilic properties, for example in mountainous terrain. This may result in reducing the risk of landslides, in improving soil characteristics, and in developing marginal areas. By avoiding the use of polluting materials produced by washing the so-called “greasy wool” during the hydrolysis process, the wool is used as a renewable resource.
- Economic: by turning wool wastes into an agricultural fertiliser the problem of the expensive disposal of a special waste is solved. The costs of transporting the product can also be reduced as the project is planning to use small on-site facilities directly in the breeding areas. The process is designed to be low-cost and without the use of chemical reagents, since no bases, acids, toxic sulphites or high-cost enzymes are used. Lastly, wool wastes from as early as the shave, greasy wool, regenerated wool or garments at the end of life can be recovered, thus increasing both the employment and the profit of ovine breeding in Europe.



Detailed study:

Nitrogen

Nitrogen is essential in any plant life process, being the specific constituent of proteins and other basic vegetable compounds such as vitamins, enzymes and, above all, chlorophyll.

Unlike animal organisms, plants carry out the synthesis of organic compounds containing nitrogen from inorganic nitrogenous materials, such as ammonium salts, nitrites and nitrates. These compounds are normal constituents of the soil, but their input is also guaranteed by special biological mechanisms in which both the atmospheric nitrogen and the excretion and decomposition products of the organisms are used (Figure 1).

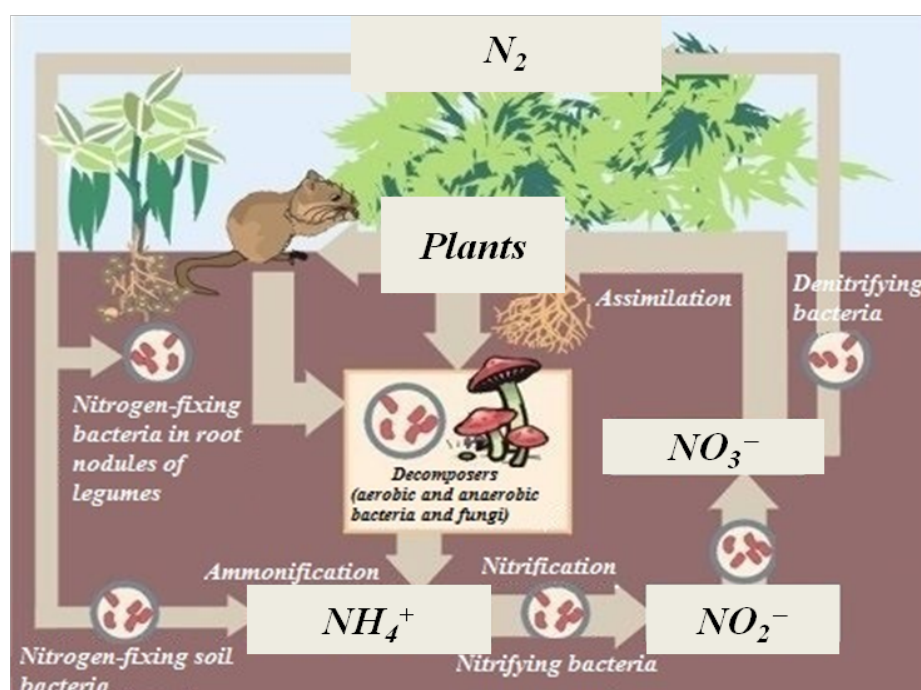


Figure 1 - The nitrogen cycle

The fixation of atmospheric nitrogen (**nitrogen fixation**) is not carried out directly by the plants, but requires the intervention of aerobic and anaerobic microorganisms present in free form in the soil, or of *Rhizobium* bacteria. The latter live in symbiosis with the roots of some leguminous plants at the so-called "nodules" and possess the "nitrogenase" enzyme which catalyses the reaction.

In nature, the transformation of elemental nitrogen into ammonia compounds occurs also by the action of electric shocks and ultraviolet radiation.



In addition to the biological or physical fixation of nitrogen, in the economy of plant metabolism, the absorption of the inorganic nitrogenous compounds present in the soil is also of great importance and the indirect input of nitrogen by organic plant and animal residues and the products living matter, decomposition is also important.

The transformation of organic nitrogen into assimilable inorganic materials (***mineralization***) takes place in the soil through a complex series of chemical and enzymatic reactions which include:

- A) The formation of ammonium salts (***ammonization***) by special microorganisms belonging to the genera *Aspergillus*, *Mucor*, *Fusarium*, etc.;
- B) The use of ammonia by autotrophic microorganisms of the genus *Nitrosomonas* with synthesis of nitrous acid salts (***nitritation***);
- C) The nitrite to nitrate transformation carried out by Nitrobacterium (***nitrification***). The processes indicated in Phases B and C together are called nitrogen nitrification. The nitrates absorbed by the plants, before being used for the synthesis of organic materials, undergo the transformation into ammonia again.

Detailed study:

Soil improvers

By this term, we mean those fertilisers that are able to improve the physical properties of the soil in order to facilitate plant growth by influencing its chemical and biological properties. Generally, materials with these characteristics are those containing clay and sand or manure, which is used to increase the humus value in the soil for an improved production action.



3. Construction industry

Thanks to its features wool is an excellent natural insulating material. In fact, since wool is highly hygroscopic, it can absorb up to 30% of air humidity, preventing steam in excess from condensing between fibers. As a consequence, less heat is lost into the atmosphere.

Wool can be inserted in the form of **insulating panels** which are suitable for aired and non-aired roofs, attics, floors, perimetric brickworks and inner stoneworks. This cladding is particularly suited for wooden structures as it guarantees a good level of air humidity.

After sheep-shearing, wool is washed with common soaps and baking soda to remove impurities and grease. Some chemical substances must be poured onto wool fibers to prevent them from being attacked by parasites, moths and insects. After carding, wool layers are stacked and pressed. By adding 20% of hemp and 10% of polyester to wool panels they become more compact and stable. To make them even more firm, after having combed the wool fibers with thin vertical needles, you can add a propylene grill. In the end wool panels can be recycled by producers.

In the last few years in order to produce eco-friendly mats and avoid the use of petroleum products, some studies have been carried out and some alternative options have been found: for instance rather than polyester, keratin can be used.

The thickness of these panels (Figure 3.4) cannot be less than 5 cm and their density must be 30 kg/m^3 . Craftsmen and skilled carpenters can insert wool inside cavity walls, garrets, plasterboard partition walls under the floors directly or by using adhesives.

Furthermore, these wool mats can absorb up to 13 grams of nitrous oxide, sulphur dioxide and formaldehyde which are polluting gases emitted by hot water heaters, traffic and cigarettes. When the toxic substances are absorbed, they are transformed into neutral substances, so this feature of wool can prevent health damage. Then since the wool structure is empty, it is able to trap air and noise. When sound waves are caught by wool, their energy is taken in and transformed into thermal energy. Therefore wool panels are suitable for rooms where echo damages sound quality.



Figure 3.4 – This picture shows rolls of wool panels. Thickness and dimensions may vary.

In figure (Figure 3.5), the artificial fibers of rockwool and glasswool, which are two different types of insulators, are shown under a microscope. These synthetic insulators are similar to wool apart from the cavities and elasticity of the latter.



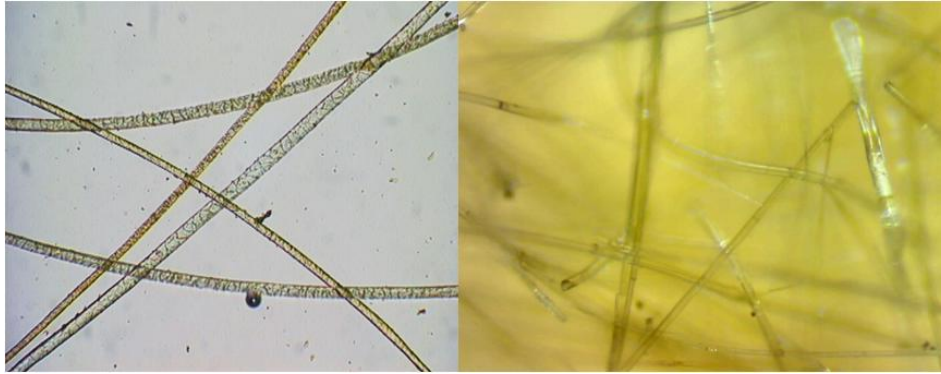


Figure 3.5 –Wool fibers on the left and glasswool fibers on the right

As a result wool is:

- a good insulating material
- long-lasting
- fireproof
- highly transpiring (absorbs up to 30 % of its weight in air humidity).

However, not all types of wool are suitable for this use. The best type of wool to use is the fleece of dairy sheep because it has a lot of keratin and lanolin.

Wool is used in the construction industry because it has a low ecological footprint and it is completely biodegradable. Moreover this use allows us to recycle wool which is too coarse and short for the textile industry. Nevertheless, there are also some disadvantages of using wool such as: the high cost of scouring, shearing and processing techniques.

In fact because of its pungent smell, greasy wool has to be washed in common washing machines adding also chemical products to make it long-lasting. This process is very expensive and the University of Camerino has shown that 4 litres of water are used to produce one kilo of wool and electricity consumption is approximately 12-18 kW for 20 kg of wool.

However, wool is really a good alternative to other insulating materials not only for its features but also for the environment. In fact Isolana™, which is one of the main producers of wool panels in Italy, states that after calculating the energetic cost of the panels it is possible to calculate the reduction for the CO₂ emissions.

It has demonstrated that if a house of 100 m² was covered with 300 m² of wool panels (each of the panels having a thickness of 10 cm and a weight of 3 kg per m²), 60 % of energy would be saved.

Furthermore, if we consider that European homes consume between 100 and 400 kwh per square metre to keep a normal living temperature, buildings where roofs are insulated with wool panels will cost 450 kwh, but they will save 6,000 kwh of energy every year.

Within a month of installing the panels they will have saved the same amount of energy that was used to install the panels along with the benefit of 2,100 kg of CO₂ and other harmful particles not being released into the atmosphere.



4. Biomedicine

Keratin is a natural, biodegradable (in vitro and in vivo) and biocompatible polymer, which can be obtained for instance from wool and transformed into materials with innovative properties. It is extracted by breaking the bonds of disulphide through the action of reducing or oxidizing agents; however, once it is regenerated, because of its low molecular weight, it has poor mechanical properties which make it difficult to use. So, there is the need for mixing it with better polymers, both natural and synthetic, with more structural properties, such as Polyethylene oxide (PEO), polyamides, silk fibroin, in order to extend its application fields.

It is possible to produce nanofibers based on keratin through the *electrospinning* process.

The equipment (Figure 3.4) consists of:

- a measuring syringe, where the polymer solution is introduced, into a capillary needle;
- a volumetric pump capable of controlling the flow in the syringe;
- a high voltage generator;
- a metal collector.

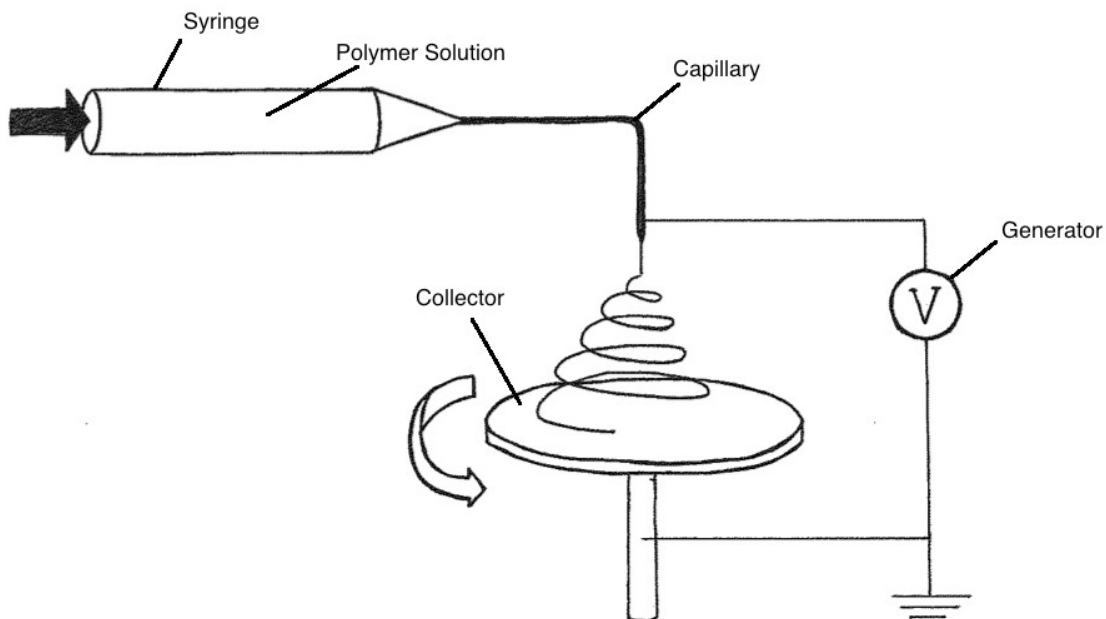


Figure 3.4 - Basic equipment for electrospinning of polymer solutions.

The polymer solution in the syringe is pumped through the capillary needle; the generator electrically charges the solution so that it is able to develop a conical shape (Taylor cone) and, passing through the electric field, it speeds up and gets thinner until a stretched fibre is created. Going towards the collector, the diameter decreases considerably because of whipping motion, in fact the movement is similar to that of a whip.



The nanofibers based on keratin, due to their characteristics, such as the high porosity, a high surface area to volume ratio, their reduced size similar to the fibrils of the extracellular matrix, have a potential biomedical application.

They could help in **tissue engineering** to produce *scaffolds*, which are supports for the cellular growth, in particular for the proliferation of fibroblasts, typical cells of the connective tissues. These supports must have some fundamental characteristics: be biocompatible in order to cause no immune reactions once they are implanted, to have a rate of biodegradability close to that of the formation of the new tissue, have optimal mechanical characteristics and have degradation products with very low toxicity. Keratin has a great potential in regenerative medicine because of the presence inside itself of important cellular adhesion sequences such as RGD (arginine, glycine, aspartic acid) and LDV (leucine, aspartic acid, valine), as well as improving the production of anti-inflammatory cytokines or reducing the pro-inflammatory cytokines.

Scaffolds should have a structure similar to the extracellular matrix and a porosity in order to allow the diffusion of gases, small molecules, metabolites, etc. necessary for living structures. Besides, it is necessary they are not colonized by bacteria that can cause infection or degrade the support. Various materials, such as cationic polymers, have been used to give antiseptic and antibacterial properties, however most of them turned out to be cytotoxic. A lot of photosensitizers exposed to short wavelength visible light in presence of oxygen, produce free radicals, like ROS (Reactive Oxygen Species), which are highly cytotoxic. Recently sponges made up of the wool's keratin have been realized, working with photosensitizers, which have demonstrated antibacterial properties, both towards Gram-negative bacteria (for example *Klebsiella pneumoniae* or *Escherichia coli*) and Gram-positive ones (for example *Staphylococcus aureus*), and also the ability to operate as a **3D scaffold** for fibroblasts' growth *in vitro*.

The **photodynamic anticancer therapy** uses photosensitizers that, producing ROS, reduce cell proliferation, induce apoptosis or necrosis, stop the cell cycle. However, a lot of these molecules have a poor specificity and as a result damage also the surrounding tissues, they are highly hydrophobic, too, and they tend to aggregate in an aqueous medium, reducing the capacity to produce ROS. Therefore, small carriers have been created capable of transporting drugs selectively towards the target tissues so that they reduce the toxicity and increase the therapeutic effectiveness. Keratin, being a protein with balanced chemical composition between polar and non-polar aminoacids, can incorporate different types of drugs; nanoparticles made up of this protein have shown *in vitro* the ability to pass through the membranes of cancer cells. In particular, good results have been obtained towards tumours like osteosarcoma or glioblastoma, by using keratin nanoparticles combined with Chlorine e6, a photosensitizer that can be easily synthesized starting from chlorophyll.

Products based on keratin are even employed as **wound dressings**. In fact, they allow breathability and create a barrier against bacteria while permitting the exchange of nutrients and gases and the transpiration of the exudates.

The healing of a wound is also obtained thanks to the ability of the keratinocytes to migrate and proliferate, an essential process for re-epithelisation. The products based on keratin have shown



stimulating effects on wound healing and accelerated the process through the stimulation of the migration of keratinocytes, their proliferation and production of proteins of the basal membrane or of the anchoring fibrils of the cellular junctions. (figure 3.7)

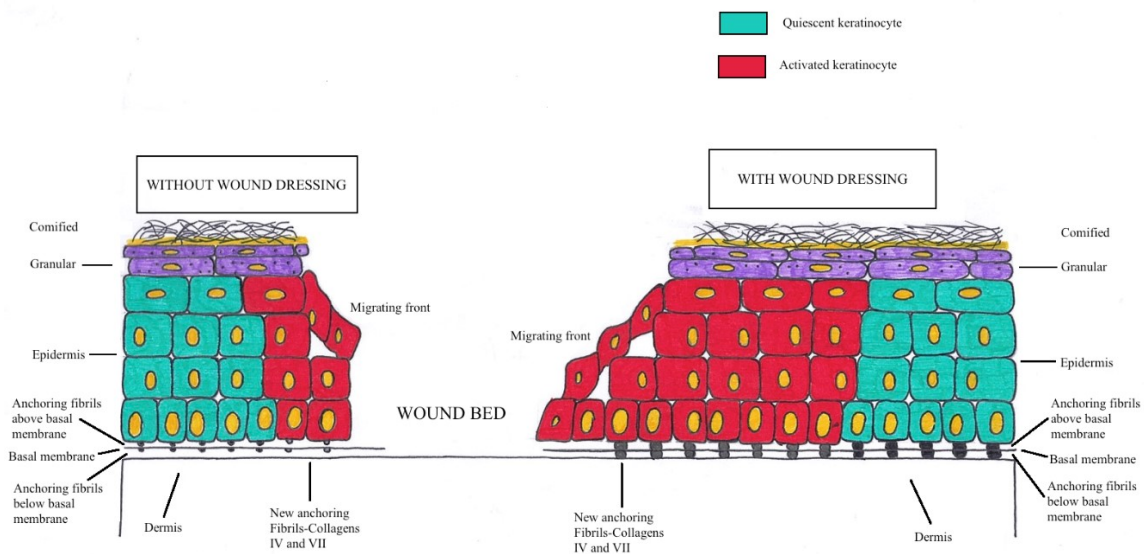


Figure 3.7 – Effects of keratin-based products on re-epithelisation.

The clinic effectiveness has been proved for the healing of ulcers, burns, skin tears, superficial injuries etc. and in particular, faster skin healing has occurred and as a result, there have been lower rate of infection and lower costs.

These products are commercialized as:

- gel;
- matrices/absorbable wound dressings rich in keratin proteins that dissolve in the wound. The traditional methods include the periodic replacement of the bandages in order to avoid the wound infection, which causes a partial removal of the stratus of epidermis formed until that moment, thus lengthening the healing process;
- multilayer dressings, in which the wound is in contact with a keratin basis supported by a highly absorbent polyurethane foam, designed for extremely exuding wounds.

As a further development of the progress made in wound healing, keratin films have been designed to make dressings mixed with blue methylene able to carry out considerable photobactericide activity against *Staphylococcus aureus* if irradiated with visible light.

Moreover, keratin nanofibres are used in the **dental field**. By covering the surface of titanium implants with them the fibroblasts' proliferation is facilitated, as well as its integration with gingival soft tissue and a reduction of bacterial penetration occurs. Therefore, the use of keratin nanofibres in the biomedical sector is expanding a lot and thanks to the great potential of the protein, it will surely develop further in the future.





5. Water purification

Water is an essential element for the development and the progress of life. Originally, in nature, water went through a series of processes (evaporation and condensation) that were sufficient to make the water drinkable, but nowadays this is no more possible.

The pollution that damages water in seas, underground, in rivers, has different origins: industrial, urban, linked to the use of agricultural fertilisers, due to the spill of hydrocarbon or other reasons (Figure 3.8). In any case, once water is polluted, in its cycle, it involves various ecosystems thus causing damage to flora, fauna and humans. For this reason, it is fundamental that humans strive to purify seas and rivers, in addition to inevitably producing polluting factors with their activities. Purification is a technological process that, making use of suitable machinery, is aimed at eliminating redundant substances and pollutants from liquid and gaseous systems. This process may be different depending on the type of pollutant. Recently technologies of bioreclamation have had great success, based on what already exists in nature and relying on living organisms in order to purify water.



Figure 3.8 - Water polluted by urban drains and oil spill.

Non-degradable products, deriving from industries, may reach the sea and accumulate in organisms causing substantial damage to them and becoming a threat to human kind; in fact, once they have reached to sea, toxic substances become part of organisms' life cycle and in addition to accumulation in their organs, moving from one trophic level to another one, they tend to gradually build up until they reach the major concentration in predators that are at the top of food chains. This phenomenon is called bioaccumulation.

Among the most toxic industrial pollutants are heavy metals, i.e. all those metallic chemical elements with a relatively high density and toxic even at low concentrations, such as lead (Pb), zinc (Zn) and cadmium (Cd). Some, like copper, are present in the body and are essential for a proper metabolism, but at higher concentrations they become toxic. Heavy metals, binding with cellular structures in which they are deposited, may hinder (the execution of) certain vital functions; for example, some of them have high affinity for sulphhydryl (-SH) groups normally found in enzymes



that catalyze metabolic functions in the body, forming a metal-sulphur complex which can cause their inhibition.

Sardinia is the Italian region that is home to one of Europe's largest disused mining sites, that of the Sulcis Iglesiente, an area close to the sea in which metallurgy developed since the time of the Phoenicians and where lead and zinc were mined until the beginning of the last century; in that area, due to deficiencies in safeguard, metals have contaminated the surrounding waters.

Drain water from houses in urban areas are another important contribution to water pollution, in particular in those cases where municipalities do not introduce appropriate purification systems before the spill into rivers or in the sea. Metals, plastics, paper and organic substances are pollutants that can cause serious damage to living organisms.

The use of fertilizers in agriculture is known to be a major cause of surface water and groundwater pollution. Large quantities of nitrates are found, for example, in groundwater in the Po Valley, as well as an excessive nitrogen load in the Po, which collects the water runoff from farm fields or from rearing farms, not law-abiding, which lead to the eutrophication of the Adriatic sea.

Another source of pollution of sea waters is oil spill in the sea. Accidental events (accidents, fires aboard oil tankers) or deliberate action (wash of oil tankers) can produce large patches of hydrocarbons that destroy the ecosystem and pollute coasts. Environmental disasters that have poured into the water a quantity of crude oil exceeding 200,000 tons occurred in 2010 in the Gulf of Mexico in an offshore platform, and in 1989 in Alaska, caused by an oil tanker. Studies show that dumping operations, i.e. connected with of daily navigation activities, cause 25% of marine pollution, against 8% caused by accidents.

To reclaim oil-polluted waters there exist various techniques, such as controlled burning, or bioreclamation which uses microorganisms able to degrade hydrocarbons, or “solidification”, i.e. the use of dry hydrophobic polymers that catch the oil and creating a rubbery material able to float on the surface of the water. However these solutions are in turn harmful to the environment and they are not suited to solve the problem quickly.

Recently the possibility of using an extremely natural and low-cost product, wool, has emerged, to purify water from heavy metals and from hydrocarbons. Raw wool is water repellent and able to absorb greasy substances up to 10 times its own weight and on this feature is based the project Biolanclean, involving the Universities of Cagliari and Sassari and a Sardegna Ricerche research promotion and technology transfer centre; floating barriers have been developed, made 100% of virgin wool to decontaminate polluted areas near harbours and industries. Natural barriers developed in the project Biolanclean are entirely natural and seem to be able to biodegrade up to two thirds of the pollution in a month; moreover, they are the first products in the world able to play the role of both absorber and purifier. They can also be used to clean up rivers from spill of fertilizers and nitrogen compounds.

Another project which aims at cleaning up the water from the so called “oil slick”, responsible for environmental disasters worldwide, is “Woolres” (Wool Recycle Eco System), funded by the region



Piedmont and promoted by Pointex (Polo di innovazione tessile). In addition to its water repellent and absorbent properties, raw wool can leave oil unchanged so that it can be re-used rather than be left to settle on the seabed with additives and it is able to play this role many times, up to 22 times. A demonstration plant has been developed, which provided very interesting results: it is thought that by using 10 tons of raw wool you can get back 463 tons of oil, cleaning up an area equivalent to 40 football fields which are 2 millimetres thick.

Both projects, Biolanclean and Woolres, use the properties of wool that is able to absorb oil but they also highlight another advantage of this fibre: wool, after being exploited fully, and therefore unsuitable for reuse, can be used as fuel in incineration plants.



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