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SUSTAINABLE ALTERNATIVES FOR WOOL VALORIZATION

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Abstract: *Use and valorization of renewable resources is a key factor within the sustainable development concept. In this context, natural fibers have known a well-deserved revival, both for clothing and non-clothing applications. During the last decades, wool production and prices has fall, due to the rise and diversification of synthetic fibers. Great amounts of wool are treated as waste and are burnt or landfilled. At present, in search for sustainable resources,wool is regarded as a biodegradable renewable resource and due to its complex chemical composition and physical structure, can find various value- added application. Two main directions to add value to wool fibers have been developed: applications that use native or slightly chemically modified fibers and applications that use the keratin biopolymer, previously extracted from the solubilized fibers. Lately, intensive research has been done on wool and its potential non-conventional applications as renewable resource. Innovative application and valorization solutions are reported in the specialty literature and different kinds of products are patented and marketed. The aim of this paper is to present the actual and potential possibilities for the valorization of native wool fibers in novel, non-clothing applications, and their contribution to the economic, environmental and social pillars of sustainable development.*

Key words:. *Renewable resources, sustainable development, biofiber, keratin, waste valorization*

1. INTRODUCTION

The history of natural fibers coincides with the history of mankind. Population growth and the development of chemical industry has driven the production of synthetic fibers, which proved to be much more easier to manufacture and process, and exhibit superior properties for certain applications.

Chemical fibers with 60 % in world fiber production in 2006 have already greatly surpassed natural fibers like cotton (38 %) and wool (2 %) [1]. The world wool production, as well as prices, has steadily declined since1990; its 2008 level, with about 1200 Mt clean wool produced, was only 20 % greater than the production of 1950 and accounted for only 2.5% of the total yearly fibre consumption [2]. As a consequence, many farmers prefer to treat the wool as a waste product and end up burning or burying it. Within the last decades, wool has become an underrated, underused resource, even if it is a high quality fiber, used for expensive textiles.

One of the main operational principles of sustainable development is the use of renewable resources of plant or animal origin. Within this context, a resurgence of interest for natural fibers and for their uses for clothing and industrial applications has been noticed. With increasing demand for sustainable materials, wool is being regarded a a renewable, sustainable, biodegradable resource, worthy of a better exploitation.

2. WOOL AS A BIOFIBER AND RENEWABLE RESOURCE

Biofiber means a natural fiber, naturally coming from a plant or animal source, which exists in nature. Wool is such a fiber and its unique properties rely on its main constituent, which is the keratin.

As a protein, keratin is made up of amino acid building-blocks, of which cystine is characteristic. Cystine, a sulphur-rich amino acid accounts for the disulfide bridges, which crosslink the adiacent macromolecules and confers toughness, resistance and insolubility to the whole assembly.

Wool fiber is an ordered collection of elongated cells, consisting of multiple types of keratin proteins. Each fiber is divided into three main areas: the cuticle, cortex, and medulla (see **Fig.1**). The cuticle is a scaly outer layer that function to protect the fiber from physical and chemical damage. The cortex is the major body of the hair fiber, which is composed of many spindle-shaped cells that contain keratin filaments. Two main groups of proteins can be found within the cortex of the hair fiber: (1) low-sulfur, “alpha” keratins (MW 40−60 kDa) and (2) high-sulfur, matrix proteins (MW 10−25 kDa). Collectively, the wool fiber consists of 50−60% alpha keratins and 20−30% matrix proteins. Keratin may account for up to 95% of the dry matter of a wool fiber. The alpha keratins assemble together to form microfibrous structures known as keratin intermediate filaments (KIFs) that impart toughness to the wool fiber. The matrix proteins function primarily as a disulfide crosslinker or binder that holds the cortical superstructure together and are also termed keratin associated proteins or KAPs .

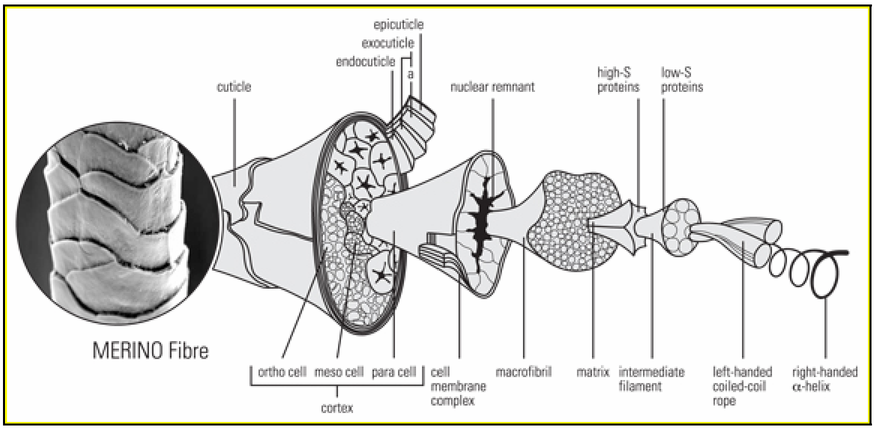


Fig.1: *Exploded view of the various structural units of the wool fibre [3]*

Wool can be considered a natural polymer matrix-fiber reinforced composite, having the most advanced hierachical organization nature has ever produced. Every year a sheep produces one new fleece, making it a renewable resource.

3. MAIN DIRECTIONS FOR SUSTAINABLE VALORIZATION OF WOOL

Valorization of wool and other keratin-based materials have been developed in two main application ranges:

- applications that make use of native fibers subjected to non-distructive, non-solubilizing treatments, such as cleaning degreasing , cutting, comminution; some mild, surface chemical treatments, such as oxidation, may be also are applied, so that the physical integrity of the fiber is not affected;

- applications in which keratin is extracted in different forms and degradation degrees from the solubilized wool fiber and is used in various applications.

The first pathway mainly makes use of low quality (coarser grades) raw wool, but also can use wool wastes coming thus avoiding the landfill or burning.

Keratin is a versatile, bioactive polymer, which became very attractive for advanced applications, from agriculture and cosmetics to bioplastics and biomaterials used in tissue engineering, regenerative medicine etc. Keratin extraction from the containing resources is a difficult task and can be achieved by chemical or enzymatic methods. An ideal solubilization should keep intact the peptide backbone and split the disulfide bond only and protect the newborn functional groups, which become available for subsequent reactions, by which added-value materials are obtained.

4. SUSTAINABLE ACTUAL AND POTENTIAL USES OF NATIVE WOOL FIBERS

4.1 Wool fibers as thermal and acoustic insulation material

Determined not only by demand for more natural building products, but also by a surplus of underused wool worldwide, sheep wool is beginning to appear as a feasible building insulation material due to its remarcable properties [4,5]. Significant properties of wool related to the insulation ability , compared with other common thermal insulators are given in **Table 1**.

Sheep wool offers a safe, natural, renewable and environmentally friendly insulation material. It is healthy as it causes no irritation to the eyes, skin or lungs and has a higher flame retardancy than cellulose and cellular plastic insulation. For best performances in terms of density and strength, wool is used in combination with other recycled fibers, usually low density polyester, in a ratio wool: other fibres = 3:1.

Table 1: *Wool properties, compared with other common insulation materials* (data from [4])

Insulation material	Thermal conductivity (W/m·K	Embodied energy (GJ/m^3)	Sound absorption coefficient (500 -2000 Hz)	Water absorption (% wt/wt)
Sheep wool	0.037	0.11	0.77 (60 mm) [5]	up to 35 %
Glass wool	0.032 – 0.04	0.83	0.65 (100 mm)	0.2 %
Polystyrene foam	0.033 – 0.035	3.03	0.35 (50 mm)	0.03 – 0.1 %

Precautions are related to the use of certain toxic chemicals during sheep grazing, which can be found in wool and the use of preservatives and antirodents (that must be applied to wool to protect it mainly if it is used in humid conditions) with potential toxic effects on humans.

Sheep's wool insulation is still a new product on the market, mainly used for the so-called green buildings [5] but a high performance, sustainable alternative.

4.2 Wool as agricultural amendment

One of the main qualities of wool is biodegradability, which means that when buried into soil, the keratin biopolymer is degraded by microorganisms and releases nutrients essential to the crops.

Wool is quite resistant to the attack of microorganisms, which are able to breakdown the keratinous fiber only in hydrophilic conditions. The degradation is obvious in terms of months: the representative functional groups of wool start to degrade and convert into biomass after 4 weeks, and in hydrophylic conditions, the weight loss is 33% in three months [6].

Because wool slowly decomposes in soil it can be used as a slow-release fertiliser, and will act as a source of nitrogen-based nutrients and sulfur over a much longer period than conventional fertilisers. Low grade raw wool or wool waste can be used as agricultural amendments, layed directly in the bottom of the planting pits , or addeed to the compost mixture, to improve the nitrogen content and water retention. Wool in non-woven form can be also used as weedmats, which initially inhibit weed growth but then slowly break down to release nutrients for the crops [7].

Experiments were done to check out the fertilizing potential of wool on the growth and yield of tomato, sweet peppper and eggplant [8]. Layers of clean wool (10 g per 1 dm^3 substrate) were inserted into the soil at 5 cm from the pot bottom, in order to force root penetration through wool. It was found that wool amendment caused changes in nutrients content of substrate and leaves and up to 33% higher yields, especially for tomato and pepper. Addition of wool or hair waste to soil increased yields of basil, thorn apple, peppermint and garden sage, increased the nitrogen content in soil and in plant tissue, stimulated soil microbial biomass.Wool acted as a slow-release fertilizer, and only 3.3 g per 1 kg of soil may support two to five harvests [9].

4.3 Wool as fiber reinforcement in polymer-fiber composites

Fiber reinforced polymer composites (FRPC) are a class of engineering materials, best suited for advanced applications such as automotive, civil infrastructure, packaging, disposable consumer products. Conventional reinforcing fibers, such as carbon or glass fibers, are expensive their preparation or use may be hazardous. Natural fibers can succesfully replace conventional reinforcement fibers and apart from using a cheap, renewable, environmentally friendly resource, they can impart some additional properties to the composite, such as biodegradability, low density, easy processability, good thermal and mechanical properties. Plant fibers, such as flax, hemp, jute, sisal, coir, pineapple etc. are succesfully combined with synthetic or biobased polymer matrices

Use of animal fibers is a solution for keratinous waste disposal. Chicken fibers can be succesfully used to reinforce high density polypropylene, for the obtaining of composites with high flexural, tensile and acoustic properties. Low fibre weight content led to better enhancement of the mechanical properties and 1-3 % wt/wt gave the best results [10].

Wool has certain applications in fiber – reinforced composite materials. It is used in native state or after some chemical surface treatments that improve the adherence to the polymer matrix.

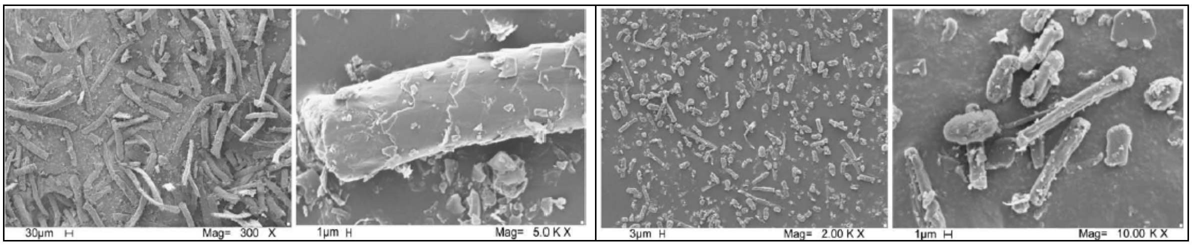
Geopolymers are inorganic aluminosilicate materials that possess relatively good mechanical properties and thermal stability but exhibit failure behavior similar to brittle solids. Strength and toughness can be improved by fiber reinforcement. New aluminosilicate inorganic polymer reinforced composites with an average fiber content of 5 % wt/wt were prepared from kaolinite-type clay and wool, previously degreased with solvents and alkalies [11]. Improvement of fiber hydrofilicity by degreasing determined a better interaction with the hydrophilic inorganic matrix, which resulted in a homogenous fiber distribution. The flexural strength and failure/fracture characteristics of the composite were improved by 40 % compared with the matrix and the thermal stability was also higher. Moreover, environmentally friendliness and relatively low cost make these composites potentially attractive for some construction applications.

Keratinous waste from a tannery, more precisely from the hair-saving liming proces, was used as a filler of synthetic acrylonitrile-butadiene rubber (NBR) [12]. The hair waste was grinded, mixed with ZnO and added to a acrylonitrile-butadien rubber. The rubber filled with 5 % wt/wt keratin fiber waste exhibited increased cross-linking density of the polymer matrix, shorter vulcanization time, improved resistance to thermal ageing and improved biodegradability. It is expected that similar waste, such as wool, will induce the same effects.

4.4 Wool powder

Wool can find promising applications by powderization, when the physical state is altered but the macromolecule structure is intact or slightly modified. Basicly, powders from natural fibers are obtained by cutting into short pieces and grinding. Due to high break and elongation strength of wool fiber, grinding is difficult and energy consuming, so certain pretreatments are applied before grinding, which reduce crystallinity and break some chemical bonds, in order to promote brittleness. By fiber comminution, some functional groups are exposed and become available for certain interactions and the specific surface increases; thus, the powder gains the characteristics of an active solid.

Wool powders can be obtained in different sizes within the micrometric range, from fine (200 -500 μm) to ultrafine (max 15 μm) depending on the grinding process parameters. For example, Xu and coworkers [13] obtained ultrafine wool powder (diameter 2 μm, length 5-10 μm, needle shape), starting from 25 μm Australian wool, by cutting in short pieces with a rotary blade (max. 3 mm) applying a mild surface oxidative treatment and grinding on a ball mill. As the powder particle size decreased, the temperature corresponding to the crystal cleavage and the destroying of the crosslinkages increased to around150°C from 120°C of the control wool fiber. Higher thermal stability



(a) (b)

Fig. 2: *SEM images of wool powders: (a) Merino wool ground on a rotary ceramic mill (medium particle size 51 μm); (b) Merino wool ground on a rotary ceramic mill, chemically treated by chlorination and milled by air-jet milling (medium particle size 4.5 μm) [14].*

suggest that the powder can be used for high temperature applications. FTIR spectra proved that no significant chemical modification of the keratin macromolecule takes place and little change of the X-ray diffraction pattern show slight change of the crystaline structure and only amorphous portions are affected.

Chemical treatment and combined milling techniques allow the obtaining of low particle sizes (see **Fig.2**) and impart new properties, such as fast uptake of anionic dyes, which was comparable to those of activated charcoal with specific surface 100 times greater [14].

4.5. Biobased films and coatings from wool powder

At present, fossil fuel-based or conventional plastics are in flagrant contradiction with the sustainable development concept, as they are obtained from non-renewable resources and, because of their low biodegradability, create substantial solid waste disposal issue . This problem has driven the development of bioplastics, a class of innovative biodegradable materials, based on biopolymers extracted from plant or animal renewable resources [15]. For certain applications, such as packaging and short service life consumer products, bioplastics will become a sustainable alternative. Keratin, due to hidrophobicity, cross-linking ability and due to the abundance of sources, is a promising candidate but the main difficulty is related to the extraction from the keratinous source. Research has been done on the use of superfine wool powder instead of solubilized keratin for the obtaining of biobased thermoplastic materials. Basicly, wool powder is thoroughly mixed with plasticizers and optionally, other syntetic or natural polymers and thr mixture is supposed to hot pressure molding.

Wang [16] mixed wool powder having an average particle size of 1.7 with glycerol plasticizer at 10 % - 50% mass content and subjected the blend to a molding pressure of 1-9 MPa at 100-160°C for 1 – 9 minutes and thermoplastic films with acceptable properties in terms of mechanical strength, tensile strength, swelling capacity, water resistance and ductility were obtained. The wool powder was intimately embeded into a continuous phase in the cross-section and the film surface was smooth. Such biodegradable films can be succesfully used for food and agriculture applications.

Ke and Xu [17] reported the obtaining of films from a blend of wool powder and chitosan, a polysaccharide biopolymer, by solution casting, which exhibited high affinity for a natural cationic dye. Incorporating natural compounds in such films can be the starting point for novel application, in food technology or medicine.

4.6. Wool-based environmentally friendly adsorbents for heavy metals.

Heavy metals are present in wastewaters coming from mining, metallurgical, electroplating, painting, textile and leather industries. They pose serious health hazard problems even if they are present in concentration lower than allowable limits, due to their bioaccumulative behavior. Conventional methods for heavy metals removal including precipitation, chelation, ion exchange are expensive and have several limitations. In recent years, there was an increasing interest in using biobased active solids acting as adsorbents, and biosorption became a viable alternative to the treatment of heavy metal contamination. Keratin fibers coming from different sources (wool, hair, feather, hooves) have proven their binding capacity of different heavy metals (Hg, Pb,Cu, Cr) in trace concentration [18,19]. The adsorption capacity of the keratin fibers is improved by chemical treatment and by reduction of the particle size, by chopping or grinding. Chemical treatment, such as alkaline treatment or treatment with chelating agents is limited to the fiber surface and aims at increasing the density of active sites.

Keratin fibers from chicken feathers, supposed to a alkaline ultrasound treatment proved a high affinity for Pb(II), Hg(II) Cu(II) and Cr(III), both in single and mixed-metal solutions [18]. The maximum uptake onto the keratin fibers mainly depends on the solution pH. Thus, the Pb removal is complete over a pH range of 4.5-5.6, while a 97.6% removal of Hg is attained at pH value of 1.9. Multiple elution and adsorption tests indicated that the keratin adsorbent can be regenerated and used in several treatment cycles.

Binding of. Co(II), Cu(II) and Cd(II) on wool powders of different particle sizes over the pH range 3 – 9 at room temperature and ion concentration ranging from 10^{-3} to 10^{-6} M was investigated [19]. The optimum pH for binding of Cu(II) and Cd(II) was in the range 6–8, while Co(II) absorption

peak was at pH 8. The rate of uptake of Cu(II) for each of the wool powder was significantly faster (~

42 fold) than that of the wool fibre. In comparison with commercial cation exchange resins, the wool powders showed higher (two to nine fold) metal ion loading capacity. The ability to produce large quantities of wool powders and their ease of handling indicate that they have potential for application in separation and recovery of metal ions from industrial effluents and environmental waterways.

5.CONCLUSIONS

Wool is one of the most valuable natural fibers, but during the last decades it has been surpasses by manmade fibers. This pushed down the prices paid for wool and many farmers around the world were forced to treat it as a waste and throw it away. At present, wool is an underrated, underused resource, despite its outsanding properties related to the textile industry.

Sustainable development is the paradigm of the present society and one of its key principles is use and valorization of accesible renewable agroresources, as an alternative to depleting fossil-fuel resources.

In a time when the finding of new resources is vital to mankind survival, a revival of natural fibers regarded as renewable, biodegradable and sustainable resources has been noticed.

Wool is such a resource and efforts have been made to find useful clothing and industrial applications, in order to resolve a waste management issue. Wool and other natural keratinous resources can be transformed into value-added products, through economically feasible manufacturing processes, which imply minimal physical and chemical transformation.

Apart from its versatile uses to consumers and industry, natural fibres are an important source of income for the farmers who produce them. Natural fibre industries employ millions of people worldwide and are of major economic importance in some developing countries. Natural fibers cultivation and valorization have a positive social impact because it assures the development of rural, agricultural-based economy and also have a positive public perception, vs. the exploitation of non-renewable resources.

Use and valorization of wool and other natural fibers into added-value products is a contribution to the environmental, economic and social sustainability.

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