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The Current State and Prospects of Recycling Silk Industry Waste into Nonwoven Materials

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Abstract: Natural fibres are the preferred options for garment, technical and medical textiles, nonwovens and composites. Their sustainability is a considerable advantage. Though, the nature of silk production and processing involves a large amount of waste. The present review explores the current issues of recycling silk waste into nonwovens for medical and air filtration purposes. The article proposes to obtain nonwovens from short fibres using electrospinning of fibroin solutions in volatile solvents. Longer fibres are proposed to be processed into needle punched nonwoven materials with a selection of an effective antistatic treatment.

Keywords: natural silk waste; dissolution; electrospinning; needle punched nonwovens

1. Natural Silk and Silk Waste

Silk is one of the oldest and most useful animal fibres known to man. Silk thread is a product of the silk-producing glands of certain insects that create a net around themselves or form cocoons. The larva of a silk moth develops by feeding on mulberry leaves and coils a cocoon with a filament 12-30 μm in diameter and up to 1.5 km long. Silkworm domestication and silk production began in China more than 5,000 years ago. A mulberry silkworm was brought to Europe in the 6th century AD.

Silk fibre consists of two proteins: fibroin is in the inner layer (72-83 % of fibre weight), which gives strength to a fibre; sericin is in the outer layer, which binds fibroin filaments together (17-28 %), there are also 0.8-1.0 % of fatty and waxy substances, 1.0-1.4 % of mineral substances and 11 % of water [1]. The amino acid profile of silk fibroin consists of 17 amino acids, most of which are glycine (43 %), alanine (30 %) and serine (12 %) [2,3].

The strength properties of silk have long been considered to be beyond the reach of synthetic fibres [4]. Silk thread with a cross-sectional area of 1 mm^2 can bear a load of 45 kg. Silk is used for manufacturing parachutes, descent space vehicles, tyres of high-end racing bicycles, and strings of musical instruments. Being a hypoallergenic material, silk is used not only in the textile industry, but also in the cosmetic industry. In addition, being biologically resistant, natural silk is used for surgical sutures and as a bioengineering material.

The largest producer of raw silk is China (50 % of the world production), with India (15 %), Uzbekistan (3 %) and Brazil (2.5 %) producing significantly less. The global volume of raw silk averages 80,000 tonnes per year and approximately 70 % comes from China. The silk industry is supported by the government and is developing rapidly in Uzbekistan, Kazakhstan, Tajikistan and Azerbaijan. Some raw silk is produced in Europe, however the demand there is still considerable. Consequently, the European market needs to import raw materials from outside the European Union.

Nevertheless, silk production has declined with the development of chemical fibres despite having significant advantages as an excellent material for garment, medical and technical textiles. Silk has been partly replaced by viscose and polyesters in the textile industry, by polyamide and aramid fibres in the defence industry. The major sericultural productions are under the threat of being closed down due to the industrialisation of Asia. However, silk continues to be one of the most important and expensive textile fibres. According to *MegaResearch*, the minimum average price for dry cocoons on the global market is USD 15 per kg. The increase in the raw silk price, which is mainly regulated by China, has a strong impact on the price of fabric and textile products.

The textile industry is one of the sectors where production wastes are up to 25 % of the raw material input. That consequently results in economic losses for companies and environmental problems. Silk production is not an exception. When silkworm cocoons and raw silk are harvested and processed, the enormous amounts of waste are produced including uncoiled cocoons, waste from silkworm cultivation, cocoon unwinding, silk spinning and silk weaving. Only about 20 % of the cocoons belong to the selected and first-quality grade and may be fully unwound having zero waste; the remaining cocoons are of the second and third grade, and are not fully processed in the silk factories. Together with the waste from silk spinning and silk weaving, the total amount of waste in all sectors of the silk industry is 55 %.

The standard classification of silk waste is based on their origin from:
- cocoon;
- cocoon unwinding;
- silk winding;
- silk spinning and weaving;
- silk dyeing and finishing.

The waste from each stage of silk production varies in terms of physical and mechanical, chemical fibre properties and geometric parameters.

The data obtained from the previous studies shows that the degree of the silk waste practical use is still low, although silk is an expensive and highly valuable product. Furthermore, the use of natural resources to satisfy human needs also requires the extensive use of recyclable materials. Non-waste technologies for processing raw materials and obtaining new valuable materials from production wastes is an urgent imperative of our time and an important area of contemporary scientific research. For this reason, scientists and engineers of different countries are constantly elaborating and improving the technologies of natural silk waste recycling both for the textile and other industries [5–8].

A part of silk winding, silk spinning and silk weaving waste is recycled with the help of the spinning equipment of related industries able to process the spinnable silk waste and produce silk yarns with a linear density of 1.5 - 5 tex. The raw fibres undergo several preparatory stages for yarn processing: they are sorted, cut, shredded, boiled and soaked to remove sericin and pupal residues, and then dried. After the preparatory phase, the fibres are loosened, stapled and carded to form a web from which the yarns are made.

The yield of silk products comprises 40-50 % of the raw material. Only 15 % of the unspinnable waste generated during the silk spinning process can be processed into a web, mainly because of the static characteristics and fibre fluffing of the fibre. The remaining waste is either landfilled or sold at a very low price outside the silk-producing countries.

Some silk manufacturers do not own the necessary equipment for recycling, and therefore pack the silk waste in 20 kg bales that are further sent for processing to countries that do not possess their own silk raw material base. Statistics show that this waste, along with the chemical fibres waste, is used to fill pillows and blankets.

The optimal way to recycle the silk industry unspinnable waste into some valuable products is to make nonwovens. Taking into consideration the hypoallergenic and antibacterial properties of silk (e.g. suitable for medical purposes) and depending on their application, it is possible to give the nonwovens some other properties as well.

Nonwovens refer to nonwoven materials obtained mainly from a fibre web, which is bonded in different ways such as stitching, needle punching, sticking, and felting. The chemical (sticking) and mechanical (stitching, needle punching, and felting) methods of producing nonwovens are widely used. The manufacturing and consumption of nonwovens is constantly growing. According to the European Disposables and Nonwoven Association (EDANA), the global consumption of nonwovens for hygienic purposes (31.9 %), construction (18.2 %), wipes (15.8 %), and filtration (6.9 %) is steadily

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increasing. The production and consumption of nonwovens for domestic use has been on the rise in recent decades.

The advantages of nonwoven technologies and materials include the possibility to use fibre raw materials of different quality, including wastes that are not suitable for spinning; high productivity of the equipment; lower production floors, labour and capital investments compared to other textile industries.

The technological process of making nonwovens generally consists of the following three steps:

- Forming the fibre web;
- Bonding the fibre web;
- Finishing of the nonwoven material.

Fibres of different chemical nature and properties, including low quality unspinnable fibres, can be used to form a fibre web. The fibre raw material is bunched, then subjected to lapping, impurity removing and mixing. These operations are quite similar to the yarn manufacturing process. After the preparatory stages, the fibres are taken to the carding machine, where a fibre web with mostly longitudinal orientation of fibres is mechanically produced. In order to reduce the anisotropic nature of the material, a cross-lapper is used by laying the web in several layers with differently oriented fibres.

Aerodynamic method for producing a fibre web is considered to be another promising option for recycling waste.

The web is then bonded using one of the following methods - stitching, needle punching, sticking, felting or a combination of them.

The final stage of nonwovens production process involves finishing, if required. The choice of a finishing option depends on the intended application. Considering physical, chemical, hygienic and consumer properties of natural silk, nonwoven materials obtained from silk waste can be used for medical purposes, production of special medical and hygienic products. Medical textiles are generally expected to have bacteriostatic or antibacterial properties. Silk fibres are quite resistant to fungi and are sufficiently resistant to proliferation of bacteria on their surface. Additionally, these properties can be strengthened by a specific bacteriostatic finishing.

2. Recycling silk waste up to 40 mm long into nonwovens

The unspinnable waste of natural silk is usually a mixture of fibres of different lengths, thicknesses and linear density. The length of the fibres is an important parameter for selecting the method of fibre web production. Staple fibres with a length of 6 to 100 mm can be processed using different nonwoven technologies. Short fibres with a length of 6 to 25 mm are generally used for paper production (e.g. cotton-silk paper). Fibres that are 100 mm long, are suitable for the production of nonwovens by means of aerodynamic method, while fibres of intermediate length can be processed on carding machines with the subsequent bonding of the web. The processing of short fibres on the carding machine results in an increased number of combings and a poor bonding of the web due to the limited number of contacts that the short fibres are able to form. If the fibres are too long, there can be issues connected with their wrapping around the carding rollers.

The developed recycling methods for short unspinnable silk waste involve the extraction of their main components, that are sericin and fibroin [8]. Prior to extraction, the waste is cleaned of impurities (dust, dirt, pupal residues), cocoon waste is also processed on cocoon cutting machines. The previous research [9,10] proposed a method of sericin extraction from silk winding waste based on aqueous solution treatment. The obtained sericin powder is further used for cotton fibre sizing that simplifies the process of blended cotton-silk yarns production. Sericin is also recovered from waste materials in the form of hydrogels that are then used during the fibre spinning processes [11].

Dissolution of waste in aqueous salt or organic solvents [12–26] and subsequent production of various medical materials from these solutions [27–33] are considered to be the most promising way of obtaining nonwoven materials from short silk waste.

In particular, nonwovens are produced from silk solutions by electrospinning to form nanofibres and laying them in a nonwoven web. A high electric voltage (5-30 kW) is applied to the forming syringe. The counter electrode (0-20 kW) is placed at a distance of 10-20 cm. A strong electrostatic field induces the repulsive forces in the charged solution, increasing the surface tension. A Taylor cone is formed at the syringe tip, and a thin polymer solution jet bursts out of the tip. The bending stress inside the jet causes it to stretch, and the solvent evaporates. A solid fibre with a diameter of 80-110 μm (depending on the properties of a solution and a solvent) is created and is randomly deposited on the counter electrode in the form of a nonwoven mesh [34]. The electrospinning method is beneficial for the production of nonwovens because nanofibres have a high ratio of their surface area to their volume. Such nonwovens are used in textile composites, high performance membrane filters and tissue engineering.

The possibility of nanofibres formation from *Bombyx mori* and *Nephila clavipes* silk solutions was first mentioned by the authors [35,36], who obtained nanofibres with a diameter of 6.5 - 200 μm from 0.23 - 1.2 % silk solutions in hexafluoro-2-propanol. However, when studying this method of obtaining nonwovens from fibroin nanofibres, it became evident that there are at least two concerns. The first one is connected with choosing a suitable solvent that should not affect the biocompatibility of the processed material when exposed to cells *in vitro* or *in vivo*. And the second one, is ensuring the possibility to adjust the supermolecular structure of the resulting fibres to achieve the optimum mechanical properties of the fibres [37].

Fibroin saline solutions are not completely viable for the production of medical materials, since the presence of salts negatively impacts both the electrospraying process and the living organism due to the deposition of calcium salts. Therefore, the solvent under electroforming conditions has to be both volatile and suitable for spraying. Many researchers are addressing these challenges and have achieved some results in applying the electroforming method to obtain nonwovens from silk fibroin solutions and its mixtures with other polymers [38–53]. Consequently, in the majority of studies silk is initially dissolved in a 50 % aqueous calcium chloride solution, then dialysed to remove the salt and to deposit. The deposited (regenerated) fibroin is then easily soluble in 98-100 % formic acid, which is used for electroforming. Homogeneous fibres with diameters of less than 100 μm are produced under spinning conditions with a concentration of 12-15 % and an electric field of 3 and 4 kW/cm. [54]. The obtained silk structures are treated with ethanol or other nonsolvent to give them a crystalline structure.

According to the patent [55] silk is proposed to be dissolved in a mixture of formic and trifluoroacetic acids at the ratio: formic acid 90-95 wt. %, trifluoroacetic acid 5-10 wt. %, an amount of fibroin from 1 to 2 grams per 10 ml of the acid mixture is further added and kept at room temperature until the fibroin is dissolved completely.

Another research [56,57] reported that aqueous solutions of fibroin can be used for electroforming. The electroforming ability is determined by the molecular mass of fibroin, the concentration, and the pH values of the solution. The conditions for electrospinning are improved with an increase in polymer concentration and its molecular mass. A pH value of 10-11 has been found to be optimal. It is likely that the nonwoven obtained from the aqueous solution of fibroin is the safest for the human body and can be successfully used as a scaffold for tissue engineering.

Summing up, the analysed studies reveal that the strength, thickness of the formed nonwoven material and the fibre diameter rise with an increase in the concentration of the solution. From the studies of electrode distance and voltage, it is found that the values of fibre diameter and tensile strength decrease with the increase of distance and applied voltage. The thinner the fibre and the material is required, the lower the solution concentration, the higher the voltage and the greater the electrode distance should be [58]. The physical and mechanical properties of such materials depend on the degree of fibroin crystallization in the solution. For instance, with an average nanofibre diameter of 375±26 μm, the tensile strength and the relative elongation at break reached 18.6±3.8 MPa and 14.0±2.5% respectively [59] which was achieved by adding ethanol during dissolution.

The electroforming process makes it possible to produce fibroin nonwoven meshes for more than just medical and biotechnological applications. Being chemically stable, nonwoven mesh is a promising filtration material that absorbs more kinetic energy than most of the other natural or synthetic fibres because of a combination of strength and extensibility. It was found that [60] silk filters reduce energy consumption for air filtration with a high filtering efficiency.

3. Recycling silk waste over 40 mm long into nonwovens

A particular feature of silk waste is that it is usually a mix of fibres of different lengths. It is common, that up to 30% of the waste fibres can be up to 40 mm long, 60% 40-80 mm long, and 10 % of the longer fibres. For such waste fibre blends, it is feasible to use a carding method to form a fibre web on carding machines, assuming that an effective antistatic fibre treatment is applied. The problem of excessively long fibres can be solved using a cutting machine. The antistatic treatment keeps most of the short fibres on the web and for the remained combings, a method of disposal is proposed, e.g. by means of a modifying agent for the synthetic fibre finishing.

The diameter of fibres in silk waste also varies significantly. The linear density of *Bombyx mori* waste fibres varies from 0.11 to 0.14 tex according to the statistical variation in fibre diameter. The staple fibres with a linear density from 0.1 to 1.7 tex are most commonly used in nonwovens. Meanwhile, the thinnest fibres are used in filtration webs because the fibre diameter has a critical influence on the pore sizes and the filtration properties of the material.

The operating principles of filter materials are based on different filtration mechanisms, including contact, diffusion and inertial capture of particles. The prevalence of one or the other mechanism depends on the type of the filter and the particles to be filtered, particle size, flow speed, etc. The dispersity of a material, which characterizes its porosity, is defined as the value of specific surface S_s representing the area of interphase surface per unit of volume or mass of the porous material. This characteristic is connected to the size of the fibres that compose the material:

$$Ss = \frac{k}{a\rho}, \quad (1)$$

where a – minimum fibre diameter,

ϱ – fibre density,

k – fibre shape factor (for rodlike fibres $k = 4$).

It follows, that the specific surface area of the material is inversely proportional to the diameter of the fibres, which compose the material: the smaller the fibre diameter, the greater the specific surface area of the material. Respectively, the larger the pores, the higher the retention capacity and the lower the hydraulic resistance. For this reason, fibre waste with a linear density of 0.11 - 0.14 tex can be effectively used not only for medical purposes but also as filtering materials. Considering the fact, that the porosity of fibrous material is determined by the total volume of voids between the structural elements, it may be assumed that the presence of silk fibres of different thickness, length and linear density in the blend would improve the filtering characteristics of the material, with all other conditions being equal. The nonwoven material obtained from waste with different geometric parameters has a more developed surface compared to the monofilament material.

For the production of nonwovens, one of the main requirements for fibre raw materials are their antistatic properties, as they allow the fibre web formation process to be carried out effectively. During the carding process, the movement and separation of fibres create an electrostatic charge on their surface. It makes it difficult to process the fibres and leads to fluffing of the fibres during carding, and to sticking to the carding machine elements. Thus, during the production of a fibrous web from silk waste it is important to consider its electrical resistance, on which depends its ability to be electrified. With a relatively high moisture capacity of silk fibres (maximum 11 %), silk does not conduct electricity well and accumulates static charges from friction. This may significantly complicate its processing. As it was estimated in the previous research [61], electrical resistance of the investigated silk waste fibres amounts to 10^{11} ohms at 20 °C and 65 % humidity that is comparable with the resistance of acetate fibres. Therefore, an essential objective of silk waste recycling technologies is the selection of an antistatic agent aimed at ensuring a continuous process of web formation on the carding machines.

The antistatic treatment is used widely in a variety of textile industry applications. Depending on the chemical structure, antistatic agents can either prevent the building up of charges or dissipate those that have already been built up by:

- reducing the friction coefficient between the fibres;
- increasing the electrical conductivity of fibres;
- increasing the dielectric permittivity of the medium between the rubbing bodies;
- changing the contact potential.

Surface active agents (surfactants) are frequently used for this purpose and can be applied together with hydrocarbons, fats, and oils in the form of emulsions. The antistatic action of a surfactant grows with the increase of polarity and depends on the hydrocarbon radical length, presence of double bonds, aromatic rings, and hydrophilic groups. Electrical resistance is most effectively reduced by ionic substances such as the salts of phosphoric acid esters and quaternary ammonium compounds. It was experimentally proved [61] that the application of cation-active quaternary ammonium salts effectively reduces the resistance of silk fibre blend by two orders of magnitude (from 10^{11} to·10^{9} ohms). In addition to antistatic agents, the use of oiling agents during spinning, and silicone agents or substances fixing the finishing agent on the fibre (polyacrylic acid, polyitaconic acid, etc.) are reported to improve the frictional properties of fibres.

The other significant cause of poor web quality might be a high coefficient of friction. The coefficient of friction at rest (coefficient of cohesion) of silk yarn on silk is 0.2 - 0.3 (in comparison, the coefficient of friction of cotton on cotton is 0.3 - 0.6). Fibre cohesion is determined by the interaction of polar groups of fibre surfaces. The washing of silk fibres from sericin, fatty and waxy substances decreases the coefficient of friction since a considerable part of silk fibre consists of nonpolar amino acids, that are alanine and glycine. The selection of antistatic treatment requires taking into account the fact that the amount of surfactant applied to the fibre affects the coefficient of friction: a monolayer of surfactant on the fibre is sufficient to block the active groups, minimizing the friction. With an increase in the number of surfactant layers, the friction coefficient begins to rise. The application of antistatic agents on the fibre blend allows reaching its content on fibre of 0.25-1.0 % by spraying the antistatic solution with 50-100 g/l concentration by means of nozzle until it reaches 5-10 % weight gain.

The task of the effective reduction of electrical resistance of silk waste without a significant increase in the content of surfactants on their surface can be solved by a bicomponent composition of surfactant and a small amount of electrolyte like sodium chloride. In this case, a surfactant creates a smooth layer on the surface of the fibre while an electrolyte provides ionic conductivity, reducing the electrical resistance of silk waste by 3-4 orders of magnitude.

The fibre web obtained from natural silk waste can be bonded using different methods. The bonding method is discussed in the scientific literature [62] and suggests pressing the fibre web into panels of a predetermined thickness for wall and interior decoration. Another research [8] presents methods of adhesive bonding of fibre webs from silk waste to produce laminated nonwovens.

Although, for obtaining medical and filtration nonwovens, the method of fibre silk web bonding by needle punching is more reasonable. This method allows obtaining a highly porous sorption-active material with a developed surface. The needle punching method enables the production of densely packed fibre systems with a random orientation of fibres.

The authors [63] obtained needle punched nonwoven from the long fibre silk waste by cutting the fibres into 60 mm pieces that had porosity parameters of 90 - 92%. It was recommended to use the material for oil spill sorption.

Research [64] states, that needle punched nonwoven materials have excellent filtering properties. Unspinnable silk fibres have different linear density and consequently different cross-sectional area, providing an opportunity to obtain nonwovens of high porosity from these fibres. Silk has pronounced surface properties primarily determined by the specific surface area, which ensures high sorption properties of the fibre materials. The total porosity of a needle punched silk material P is determined by the formula:

$$\boldsymbol{P} = \frac{\rho - \rho_m}{\rho} \cdot 100\%, \qquad (2)$$

where ρ - silk density, kg/m3;
ρ_m - material density, kg/m3,

and reached 97-99 %.

For the silk fibres having a shape, which can be approximated in the simplest case by a cylinder, the specific surface area A_s can be calculated according to the formula:

$$As = \frac{2}{rp}\frac{l+r}{l}, \qquad (3)$$

if $l >> r$

$$As = \frac{4}{rp}, \qquad (4)$$

where l, r - length and cross-sectional radius of the fibre, respectively.

Distribution of sizes of micro- and mesopores of needle punched nonwoven material from silk waste, according to the results of low-temperature nitrogen sorption data processing, is bimodal, i.e. the material contains both micro- and macropores playing different roles in filtration processes: large pores of 200 - 250 μm provide a high value of pore volume and total air permeability, smaller mesopores and pores up to 100 μm provide effective particle retention during filtration.

Needle punched silk nonwovens have a high air permeability and water vapour permeability under the influence of differential pressure. This ability depends on the production technologies in terms of surface density, needle punching frequency, thickness, bulk density and material filling with fibre are determined by the formula

$$B = b\,\frac{1}{Ef \cdot L}, \qquad (4)$$

where b - coefficient that is equal to 11,68 dm^3/(m·s) for needle punched materials,

E_f - material filling with fibre,

L - material thickness, m.

Aerodynamic resistance of needle punched silk materials is dependent on the modes of needle punching and the surface density. For needle punched webs with a surface density of more than 500 g/m^2 insignificant changes of their bulk density lead to a significant increase of aerodynamic resistance of materials. This dependence is less pronounced for materials with lower surface density. Consequently, the bulk density value may be used as a structural parameter of the material.

Silk nonwovens obtained from waste are stable by size and have a developed surface area. They also have high particle retention capacity and are capable of long lasting and efficient air filtration to clean the air of dust, fly ash, fine sand, cement, ultrashort textile fibres and other pollutants. As we showed in [64], the filtration capacity of needle punched silk waste nonwovens against particles of typical air pollutants is close to 99.9 %.

The prominent feature of silk is that it stands out from other natural fibres because of its superior resistance to abrasion, bacteria, and fungus. Therefore, there is an ongoing interest in exploring the possibility of using nonwoven silk materials for medical purposes. Natural silk is an immunostimulating, hypoallergenic and antibacterial material. It positively influences on human body because its products help to maintain normal moisture and temperature balance on skin, help to relief or reduce irritations and inflammations. Methods of finishing the material with antibacterial agents have been proposed to enhance antibacterial properties.

Textile materials with antimicrobial properties started to be developed in the nineteenth century. Nowadays, there is already a sufficiently broad range of materials with antifungal and antibacterial properties. Nevertheless, research in this area is constantly evolving. The considered materials are of particular interest due to the development of drug resistance of bacteria as a result of adaptation of microorganisms to antibiotic therapy. Indeed, research into antibacterial materials, including textiles, continues to grow. According to the World Health Organization, between 20 % and 40 % of diseases are infectious. The SARS-CoV-2 pandemic has also fostered the focus on antibacterial materials. As a result, antibacterial treatment of biomedical textiles has become an important area of study and one of the fastest growing sectors of the textile market. The production output in this area is growing at an average annual rate of 12 % and is close to 4 billion dollars.

Antibacterial properties can be given to a textile material in different ways. Antibacterial agents can be applied to a textile material at the final stage of finishing by means of impregnation. In the

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case of synthetic fibres and polymers, antimicrobial agents can be added to the polymer composition, or to a spinning solution, or during the formation of filaments. Antibacterial finishes used in the textile industry include bactericides of both organic (phenols and their derivatives, amines and their salts, heterocyclic compounds, organo-element compounds, etc.) and inorganic nature. Silver, gold, platinum are widely known for their antibacterial properties and are widely used in the production of fibrous composites for medical, sport and hygienic purposes. These metals possess pronounced antibacterial, antiviral, antifungal and antiseptic action against a number of pathogenic microorganisms capable to provoke various infectious diseases. Recently, this class of compounds has been of great concern due to the discovery of the possibility of using minimal concentrations of toxic metals in their nanoscale form.

Textile finishing with nanoparticles involves impregnation of the fibrous material with a previously prepared nanoparticle solution containing an additional stabilizer to prevent agglomeration. Alternatively, metal ions adsorbed by the fibrous material are chemically reduced by treating the material with solutions of metal salts. If the first method is chosen, colloidal dispersions of silver nanoparticles containing at least one stabilizer to prevent agglomeration of the nanoparticles are used.

The second method involves the impregnation of fibre or textile material with a solution of metall salt followed by the addition of a reducing agent or without adding [65]. In this case, nanoparticles are formed directly on the fibre, their size is controlled by the concentration, type of reducing agent, the size of pores of the fibrous material, etc.

Silk fibre and its needle punched nonwovens have a developed inner surface with pores and voids, through which metal nanoparticles can penetrate and attach effectively because of physical and chemical sorption. Therefore, the nonwoven material serves both as a nanoreactor for nanoparticle synthesis and as a stabilizer, limiting the growth and aggregation of particles. Fibroin functional groups can serve as centres of ion sorption and nanoparticle nucleation.

Studies [66] have investigated the influence of reducing agents of different nature (hydrazine sulfate, methol, borohydride, and sodium hypophosphate) on the size of silver nanoparticles applied to the natural silk waste material. The technological parameters of their application process were optimized using mathematical algorithms [67]. The antibacterial and fungicidal properties of silk fibre waste materials were tested. It was found that even 1 % of silver nanoparticles in the silk fibre material ensures its antibacterial and antifungal effect, while bimetallic Ag-Cu nanoparticles exhibit synergistic effect. The strength of metal nanoparticle attachment in the porous structure of silk waste nonwovens is detected by FTIR, as a physico-chemical interaction between the active groups of fibroin and a metal, while the size of the nanoparticles is stabilized by the pore size of the material.

Conclusion

The processing of valuable natural silk raw material is characterized by the fact that it generates up to 50 wt. % of waste. Despite the intensive research on this subject, at the moment no total silk waste recycling technology has been achieved. Part of the waste can be recycled by the silk spinning process, the remaining unspinnable waste can be efficiently used to produce nonwovens.

Waste in the form of short fibres and combings could be potentially processed into nonwovens through electrospinning, followed by laying of nanofibres in fibre webs. In the majority of cases this is achieved with the use of nontoxic volatile solvents.

Longer fibres are processed using traditional nonwoven technologies. It is worth mentioning, that the selection of an effective antistatic treatment is crucially important for obtaining even, anisotropic webs. The analysis of the main methods of producing nonwovens (sticking, felting, needle punching, stitching) allows offering needle punching technology as an optimal way of obtaining nonwoven material from silk waste.

The properties of natural silk fibres such as hypoallergenicity, resistance to bacteria and chemical stability make them suitable for medical and hygienic purposes, as well as for air purification as filter materials.

The method of attaching nanoparticles of metals (silver, copper) to the porous structure of a nonwoven by chemical reduction from aqueous solutions of salts has been developed to give additional antibacterial properties to the nonwoven material made of silk waste.

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