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NANOTECHNOLOGY - NEW TREND IN COSMETOLOGY?

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S u m m a r y. Nanoparticles used in cosmetic preparations and drugs used on the skin are probably capable of overcoming the skin barrier. Titanium oxide (IV) easily overcomes this barrier without penetrating the deeper layers of the skin. It is possible to accumulate nanoparticles in the hair follicles [14]. In addition, nanoparticles can cause inflammation and damage to animal tissues [2]. As a result of exposure to nanomaterials, oxidative stress in the body can be triggered. This may result in the formation of free radicals and their pathological impact on the body [27]. A precautionary matrix has been introduced in the European Union. Its aim is to increase responsibility in applying the precautionary method. It facilitates the identification of probable sources of risk when using nanoparticles [3].

K e y w o r d s: nanoparticles, nanotechnology, liposomes, nanoemulsion, nanometals

INTRODUCTION

The term ‘nanotechnology’ pertains to the research and use of molecules that are the size of atoms and macromolecules. The prefix ‘nano-‘ is of Greek origin meaning ‘a dwarf’. Nanotechnology is based on the nanometric scale. The appearance of nanoscience and nanotechnology dates back to 1959, to physicist Richard Feyman. Nanoparticles are the elements whose dimension is not more than 100 nm (some sources give a limit of 250 nm), which also demonstrate properties not shown in a larger size. Additionally, it is possible to create a nano-size object and use it [14]. Nanomaterials are characterised by prolonged release, protection of unstable chemical groups from degradation, low toxicity aside the control of skin permeability [28, 29]. Two methods are used to create nanoparticles, i.e. top-down and bottom-up. The top-down method has been used for a long time and is based on abrading the material to a very fine form. It is based mainly on mechanical processes, lithography and ultra-precision techniques. Mechanical processes consist in mechanical crushing of materials, usually grinding or cutting, which is associated with a change in the material structure. They carry many advantages and disadvantages that make them less used.

The lithographic process involves two stages: 1) composing the pattern on a given material, using ultraviolet radiation, ion or electrons beams, 2) acid-etching to remove the altered material or build up another one [15]. The bottom-up method consists in creating larger structures from individual atoms or molecules by chemical synthesis, which can be:
1) chemical synthesis in the liquid phase,
2) chemical synthesis in the gas phase [15].

The former uses sol-gel method. The desired features include: the purity of the products obtained, simple methodology, the ability to control production to create a product of desired properties. These methods are used to create transition metal oxide nanoparticles. First, a salt of a given compound by hydrolysis is obtained, and subsequently the sol is heated to obtain pure compound. Precipitation methods are found in this group [15].

The latter type are chemical deposition techniques, i.e. chemical vapor deposition (CVD), aerosol pyrolysis - spray pyrolysis deposition SPD). In CVD technology, the precursor is in the gas phase and the synthesis takes place in a gaseous form. The SPD method proceeds in a manner similar to the chemical deposition, with the difference that the aerosol is formed from the precursor solution, and then it is transferred to the surface where the synthesis takes place. [15] In this group, the self-organization technique is still present. It is characterized by spontaneous formation of nanostructures from atoms and molecules. As a result, fullerenes and nanotubes are formed [14].

Nanoforms: liposomes

The name 'liposomes' refers to nanostructures made of phospholipids [18]. Liposomes are very common and constantly perfected nanostructures. Their discovery dates back to 1961, to British haematologist D. Bangham. They consist of lipids typical of biological membranes. Their great advantage is that their structure supports the transport of active substances via transepidermal route, which affects the regulation of water and fat management. The structure of liposome is based on the construction of micelles. The liposome's interior is made up of hydrophilic substances, while lipophilic substances are found on its external layer. These molecules, therefore, take spherical membrane forms. It is possible to apply water or hydrophilic components onto the internal membranes layers, and lipophilic substances onto the external one. The structure in the form of two membranes allows for placing active ingredients inside the liposomes, e.g. vitamins [14]. The raw materials used for the production of liposomes are: lecithin, pharmaceutical glycerine, and biologically active ingredients such as vitamins, or active substances like proteins, plant extracts, humectants [5].

Lecithin classified as water / oil emulsifier is an important representative of surfactants, and amphiphilic compounds. It works perfectly in contact with the skin. It does not cause irritation, oils the skin and makes it more elastic, supports the absorption of active substances into the skin. Lecithin is a mixture of polar and non-polar lipids. The polar fraction is composed, in particular, of phospholipids and glycolipids. The application of phospholipids is very beneficial, mainly due to the high content of polyunsaturated fatty acids. They are responsible for the regulation of skin defence and increase the amount of linolenic acid in the skin. In addition, lecithin binds water, and by occlusion on collagen fibres it retain moisture for a longer period of time [5].

Pharmaceutical glycerine, on the other hand, is a colourless thick liquid of high viscosity, well soluble in water, hygroscopic, and non-toxic. It comes from saponifying fats or is synthetized from propene. Glycerine is included in emollients, creates an occlusive layer on the skin, preventing excessive loss of water from deeper layers of the skin, and protects against adverse external conditions. Therefore, it is an important component of emulsions, where it ensures protective coat for the skin [5].

Biologically active substances, mainly vitamins, have a beneficial cosmetic effect. Vitamins are biocatalysts, possess diversified structure, and influence body functioning. When applied onto the skin, they produce excellent results. They delay the aging of the skin not affecting natural processes in the skin. The spread of vitamins in the skin depends on the substrate used to manufacture cosmetics. This is determined by vitamin solubility in fats, i.e. vitamins A, E, F, or in water, e.g. vitamin C. Not only are vitamins contained in liposome forms, but also proteins, plant extracts, and highly moisturizing substances. For the skin to be able to use these substances, they must reach its deeper layers in an active form. It is achieved due to liposomes [5].

Liposomes form spontaneously from phospholipids in aqueous environment, and are filled with a small amount of water. They come by forming spherical forms in the aqueous-vesicular systems in the obtained lecithin fractions. These spatial forms are arranged in single or multi-layered structures, where the hydrophilic layer surrounds the hydrophobic one [5].

There are several methods for making liposomes:

- movie method;

- injection from an alcoholic solution method
- extrusion technique [5].

Liposomes can be divided into four main classes (due to the number of layers that build them):

- multi lamellar lipid vesicles (MLV) - 200 nm - several microns
- small unilamellar lipid vesicles (SUV) - 25-100nm
- large unilamellar lipid vesicles (LUV) - 100-400nm
- huge bubbles (giant)> 1 micron [16].

However, in terms of lipid properties of the encasement, liposomes are classified as:

- neutral - consisting of phospholipids and cholesterol;
- positive - composed of phospholipids, cholesterol and cation (ethyl trimethylammonium bromide);
- negative - made of phospholipids, cholesterol and anion (phosphatidic acid, triacetylphosphate) [18].

The classes of liposomes differ in structure and the size of water space enclosed in the liposome. The selection of the obtaining method depends also on the type of these structures [16].

There are several advantages of using liposomes in cosmetics. They reach the deeper layers of the skin, including the dermis, allow penetration of active substances into the skin without changing their form. They are also compatible with cell membranes and allow controlled release of active substances. They prevent interactions between compounds and enable the application of an active substance in higher concentration without adverse effects [17].

Physicochemical properties of liposomes: stability

Surfactant compounds influence the stability of liposomes through the degradation of their membranes. O / W type emulsifiers also work unfavourably, re-orientating the surface charge, which reduces hydration and hydrolysis of phosphatidylcholine. It results in an increase in fluidity and membrane permeability, which may involve the association of vesicles and the leakage of active substances. In addition, an auto-oxidation process may occur, i.e. the disintegration of the lipid sphere leading to the degradation of phospholipids [18]. As a result, harmful compounds are produced. The liposomal fluidity of the bilayer membrane is affected by cholesterol. It regulates the effect of temperature changes, prevents the bubbles from aggregation. Another method to counteract auto-oxidation of liposomes is to surround them with a biopolymer membrane. Chitosan, which forms a covalent crosslinking on the surface of the liposome without changing its structure, is used for these purposes. The use of this polymer to facilitate the release of the active substance from the follicle is an advantage. Stabilization of liposomes occurs due to gelling agents added to the emulsion. These nanostructures are stable at pH 5.5-7 [7].

Colloids

Liposomes have the character of colloids. According to the state of aggregation they are divided into sols, aerosols and emulsions. Their kinetic stability is the result of electric charge on the surface of particles. The value of electrical potential is inversely proportional to the increase in ionic strength. The colloidal system is stable over time, and the aging processes run very slowly when the potential is not changing, and has high absolute value. Coagulation and flocculation processes may occur. Coagulation occurs by combining the dispersed phase molecules into larger, irregular aggregates. Flocculation precedes coagulation. In these systems, the Brownian motion can be noticed, i.e. dynamic, disordered, vibrating movement. In addition, the Tyndall effect is observed, i.e. as a result of a light beam passing through the solution, it deflects, disperses and takes the form of a light cone.

Application of liposomes in cosmetics

The first cosmetic produced by liposomal technology was implemented by L`Oreal and Dior in 1987. The manufacturers used liposome particle size of 100-300nm. Liposomes exhibit similarity to the cell membrane, thereby they deeply penetrate the skin. This allows active substances be placed inside the bubbles to be inserted beneath the surface of the skin. In addition, they protect active substance against damage by the external environment and enzymes. Liposomes are completely biocompatible and biodegradable. They perfectly

affect the corneum layer of the epidermis, i.e. they nourish, strengthen, maintain water-lipid balance, and protect against drying of the skin. Introduction of active substances inside the liposomes is possible thanks to the 'microencapsulation' technique [18]. Encapsulation is a method by which one material or mixture of materials is coated or encapsulated inside another material or system. The beginnings of using this process are attributed to the 1950s. The technique is used to encapsulate fats, oils, fragrances, oleoresins, vitamins, minerals, enzymes and dyes. These are diverse structures larger than 1000 μm. Some have a spherical shape with a continuous area of the core and shell, the other are irregularly shaped with a large number of small droplets or particles of core material. Encapsulation methods are divided into: chemical processes and physical or mechanical processes [1].

Nanocapsules are used in cosmetics. These are vesicular systems with active substance in the core surrounded by polymeric coating or is absorbed on its surface. Encapsulation is easily made with lipophilic substances, which show biocompatibility of the coating and by-products, as well as biodegradability of constituent substances. Chitosan or cyclodextrin are the polymers used to encapsulate the core substance. The advantage of nanocapsules is their ability to control the release of active ingredients due to free enzymatic degradation of the coating polymer.

Other forms of nanocapsules are polymerosomes, colaspheres and nanospheres. Polymerosomes are similar to liposomes. However, only polymerosomes are used to transport water-soluble active ingredients. The colaspheres are fully degraded structures, because they consist of building materials naturally occurring in the skin, i.e. collagen and glycosaminoglycans. However, nanospheres are solid, colloidal particles [7]. Liposomes and other derived carrier forms find their application mainly in anti-aging products and formulas for dried skin [12].

It is also possible to use empty liposomes. They support epidermis renewal processes, improve its elasticity, allow treatment of acne lesions or support the penetration of ingredients such as DHA [18]. Together with liposomes, there is the possibility of penetrating harmful substances into the skin, which may result in skin diseases or cancer. It is important, therefore, that liposome-containing preparations should be applied overnight on cleansed skin. These cosmetics are addressed to mature skin that needs regeneration so they are not recommended for women under 30 years of age [18].

Cosmetic preparations containing components created as a result of liposome technology include: skin care creams, creams-gels and after shave balms, self-tanning, stretch marks oils, bath lotions, sauna preparations, and non-alcoholic tonics [18].

Apart from liposomes, there are other carrier systems used in cosmetology. Niosomes have similar features to liposomes. Their big plus is higher durability. They are synthetically obtained from non-ionic active substances. Sphingosomes are of animal origin and are more stable and durable than liposomes. They perfectly regenerate the epidermis.

Noctosomies are used in night-time preparations. Marinosomes contain an extract from natural marine organisms. Those are used in the treatment of skin diseases. Ethosomes are composed of phospholipids, ethanol and water, which strengthens membrane elasticity and enhances penetration of the skin. Nanoparticles carry lipophilic active substances and have the ability to penetrate deep into the skin [18].

Nanoemulsions

Nanoemulsions are characterized by transparency and homogeneity. It is a water-oil system based on specific surface-active compounds. Among the ordinary emulsions, they are distinguished by the degree of disintegration of the dispersed phase, at least one rank smaller, and correspond to the size of particles of colloidal systems.

Nanoemulsions are extremely easy to obtain. They are manufactures by mixing previously composed phases at appropriate temperature. A thermodynamically stable product is obtained. It is not subjected to creaming or sedimentation so it perfectly transports active substances. Nanoemulsions offer product aesthetics, transparency, high fluidity, and low viscosity. As a result, they are an excellent base for cosmetic products, and are commonly used in anti-aging preparations [13].

Nanosponges

They are porous polymeric structures of 10-800nm particle size. Monomers cross-linked in

the emulsion make up the form of micro compartments. They are characterized by the absorption of active compounds into the pores of spongy structures. Their drawback is the lack of release control and lack of protection of absorbed active ingredients [8].

Colasheres

Nanocarriers are composed of biogenic substances, i.e. collagen and glycosaminoglycans. There are two types of capsules [8]:

- H-thermometers transporting hydrophobic substances,
- A-shafts carrying hydrophilic components.

They are characterized by biodegradability, high bioavailability and pleasant sensations during application [8]. SLN (solid lipid nanoparticles) is the first generation of lipid nanoparticles. They are produced by replacing liquid lipids with an O / W emulsion in favour of solid fats or a mixture thereof used as emulsifier. A matrix of solid lipid particles is obtained at room temperature as well as *in vivo*. Although they are widely recognized as safe, they have some limitations, which is their relatively small loading capacity compared to many active substances. Active substances are suspended or dissolved in the lipid matrix [13, 30, 31].

NLC (nanostructured lipid carriers) are an improved form of carriers of the first generation SLN. They are manufactured by using mixtures of solid and liquid fats. They have a lower melting point but remain constant at the temperature of the human body. It increases their load capacity, and also reduces the risk of premature expulsion. Nanostructured lipid carriers are more stable than solid lipid nanoparticles [13, 32].

Nanometals

Nanometals, currently widely used in cosmetics, constitute a group of mined metals up to the nano scale [13].

Silver

Argentum, silver, is a metal showing bactericidal properties. It attacks microorganisms via catalytic oxidation, protein denaturation, DNA and cell wall damage. Its main advantage is that microorganisms do not develop resistance to silver. Its effectiveness reaches 99.9% against bacteria and fungi. The properties of silver were already used in antiquity. Today interest in silver has been revived by nanotechnology. Silver is safe and relatively cheap. The nano size enhances biocidal properties of silver, so does resistance to organic and inorganic acids. The mechanism of functioning results from the toxic action of individual nanosilver ions on microbial cells, which is based on the oxidation of the genetic material of the cell. A silver molecule is capable of absorbing oxygen and participates as a catalyst in oxidation processes. Oxygen accumulated on the silver surface reacts with thiol groups thus preventing bacteria from respiration due to blocking the electron transfer channels. Mammalian organisms are not susceptible to silver because they do not have peptidoglycans in their structure. Colloidal nanosilver may be an alternative to traditional antibiotic therapy. It kills more than 650 different bacteria while standard antibiotics roughly 10. No undesirable side effects have been observed. Silver solutions are used externally to wash various skin lesions, treat difficult to heal wounds, instil eyedrops and nose drops, or used as mouth rinses. It is used for disinfection, pest control of rooms, air-conditioning, saunas, swimming pools as it is less irritating than chlorine. Nanosilver is used in the cosmetic production process, where it increases the product quality as well as fungicidal and bactericidal properties which makes it a perfect solution for people with bacterial skin infections [13]. Products containing nanosilver are ideal for allergy sufferers due to their odour and chemical purity, and for diabetics owing to their delicacy and prevention of infections. However, nanosilver should be used with caution as it has not been fully tested [5].

Gold

Aurum, gold is a metal insensitive to external factors and most acids. It is characterized by low chemical activity. Its healing properties were already used in ancient China, while in Europe much later, from 1890, thanks to Robert Koch. Gold is perfect for use in medicine because of no toxicity and side effects. The properties of nanogolds differ from gold at the macro scale. They are easily introduced into the body due to their solubility in water or other liquids.

The condition for proper dissolution of gold is to crush it into gold dust, which should be transformed using thiols. This technique allows

the introduction of antioxidants along with nano gold during cosmetic treatments. Another method of creating nanogold particles is the reaction of tetrachloroauric acid (III) with citric acid. This is a colour reaction. Small particles have dark-red colour, which in larger particles in solution turns from pink through purple to blue. This is observed because the electrons of the nanoparticles start to vibrate in the same direction when transmitting the beam of light visible through the colloid.

Nano-gold can transport drugs to the body, acts bacteriostatically, bactericidally, and is a catalyst of chemical reactions. In cosmetics, the gold nanocolloid helps stimulate collagen synthesis and revitalizes the skin. The non-ionic colloid, on the other hand, applied externally prevents the aging processes, so it is used in skin cleansing, treatment of abscesses and other inflammatory conditions. In addition, it is used in the treatment of burns, as an anti-inflammatory, anti-allergic agent, and it positively affects the cardiovascular system [13].

Zinc oxide

Zinc oxide has the ability to absorb ultraviolet radiation in the range of 280-400 nm. That is why it is often used in creams and sunscreens. Natural zinc oxide is white and opaque, which is not observe d when nanoparticles of this compound are used. ZnO in the form of nano is produced mostly by chemical vapor deposition, hydrolysis or flame synthesis. Tests and studies on toxicity of zinc oxide are ongoing. These molecules have been shown to exhibit toxic effects on the epithelial cells, alveolar macrophages and nerve cells.

There is also the likelihood of ZnO producing reactive oxygen species in the human body, which can accelerate aging, skin cancer, DNA damage, and apoptosis. The biggest hazard occurs when zinc oxide nanoparticles have been inhaled. It may cause a metallurgist fever. To reduce the risk of ZnO nano-objects, the researchers have developed ‘encapsulating’ of base particles using an amorphous silica shell.

This compound is perceived as safe, non-toxic in small and medium doses and thus safely used in cosmetic preparations. The cosmetics with UV filters produced are not only safer but also more effective [19].

Platinum

Platinum is a silvery-white precious metal which catalyses many reactions. Its properties are widely used in many fields. Platinum compounds are used in chemotherapy, for example in leukaemia treatment. The platinum nanocolloid is used externally. Dermatology and cosmetology make use of its whitening and rejuvenating effects, reducing age and liver spots. It has toning and moisturizing properties. It provides radiant appearance and firmness of the skin. The colloid can also be used in the gel form, which has a beneficial effect on the skin, e.g.it improves skin condition, increases its firmness, reduces erythema and diseases of allergic etiology [13].

Copper

Cuprum, copper, metal valued for its properties as early as in prehistoric times. Copper nanoparticles have the strongest antifungal properties. In addition, copper stimulates the hematopoietic system, supports the metabolism of iron, is a cofactor of vitamin C oxidation reaction, favours the development of the nervous system. It is an element that builds antibodies against many diseases. In external cosmetology copper has many uses. It improves the skin and hair condition, helps treat fungal infections and skin ulcers, eliminates free radicals and thus prevents the processes of aging. Copper nanocolloid used in cosmetics has antioxidant, anti-aging and neutralizing properties of free radicals, revitalizing and immunostimulating. It is mainly used in deodorants to reduce excessive sweating and neutralize unpleasant odour of sweat [13].

Carbon nanomaterials

The following carbon nanomaterials are used: graphite, diamond, fullerene [20]. Carbon nanotubes are widely used. The world heard about them in the 1990s. Many of them are obtained by rolling up the graphene structure. They are characterized by good thermal and electrical conductivity. They can take the form of a deposit made of twisted, sticky, mixed nanotubes or rows of parallel nanotubes. There are several methods of obtaining them [20]:

- electro-stress method,
- laser ablation method,
- chemical vapor deposition method,

- others like electrolysis, flame method, grinding in ball mills.

Carbon nanotubes are one-dimensional. They are characterized by a wide range of temperature stability. They are among the most durable materials, resistant to bending, bulging, and light [20]. In cosmetology, graphene, fullerenes and carbon nanotubes are readily used. It has been shown that fullerenes are safe for the body, which facilitates their use in the production of cosmetic preparations. It was found that these nanomaterials can stimulate hair growth. This is likely due to fullerene absorption of free radicals, which contributes to the protection of hair follicles. Antioxidant activity of these compounds has also been shown, which makes them readily used in skincare preparations. Carbon nanotubes, on the other hand, were used in the mixtures for colouring hair and eyelashes. The formulas were used in the production of mascara with reinforced effect [6].

Application of nanoparticles in cosmetology

Recent years have brought a nanotechnological breakthrough in cosmetology, especially in the production of cosmetics and beauty treatments. New preparations containing nanocapsules, niosomes or nanoemulsions have appeared on the cosmetic market. These structures are used in moisturizing creams, nourishing creams, hair care preparations, sunscreen cosmetics and self-tanning products. Active substances in the form of nanoparticles penetrate the skin more easily and reach deeper layers, affecting them. Nanoforms are more effective in creams and other formulations as they are released in target places.

In UV-protecting formulations, nanostructures absorb ultraviolet radiation and eliminate reactive oxygen species [13]. Most often, nanoparticles are used in moisturizing preparations due to their structure similar to the lipids of the epidermis. Nanocapsules, colaspheres, liposomes, nanospheres, SLN, NLC and nanoemulsions exhibit numerous activities in moisturizing cosmetics. They transport moisturizing substances (hyaluronic acid, collagen), regenerate the epidermal barrier, and form an occlusive layer. Conditioners contain ethanolosomes, nanocapsules, nanoemulsions, nanosilver and nanomaterials.

They transport active, smoothing, nourishing and regenerating compounds, demonstrate antibacterial and antifungal properties, as well as spread the aroma. Nanomaterials are used in radiation protection. They eliminate bleaching of the skin after preparation application, increase durability and effectiveness of the preparation, and reduce irritation and allergy. These preparations include chemical filters - nanocapsules, nanospheres, SLN, NLC and physical-inorganic nanoparticles of titanium dioxide and zinc oxide.

Most often, nanotechnology is used in the production of anti-wrinkle products. They include: antioxidants - SLN, NLC, liposomes, nanoemulsions, nanocapsules, nanospheres, vitamin A and its derivative - SLN, liposomes, nanocapsules, vitamin K- nanosomes, elasticising substances - liposomes, nanocapsules, anti-wrinkles - liposomes and nanocapsules [7].
Silver nanoparticles is another group of nanostructures included in cosmetics. The bactericidal properties of nanosilver are used in antiperspirants, face and foot creams, hair shampoos and shower gels.

The encapsulation method is used to increase the stability of cosmetic products. It results, among others, in liposomes production, allowing the transport of active compounds to the place where they are needed. A similar task is fulfilled by solid lipid nanoparticles (SNL) [10]. The nanocapsules protect active substances against degradation, which affects better absorption of these ingredients by the skin.

Silver and copper nanoparticles can be an alternative to preservatives. They can be found in oral hygiene dentifrices [14]. In addition, nanosilver ions are used in the production of disinfectants and ointments for external treatment of wounds or burns. They exhibit less toxicity than silver nitrate and do not cause skin discolorations [21, 22]. Similarly, some creams and body lotions contain nanoemulsions [14].

CONCLUSIONS

In cosmetology carbon nanotubes find application as antioxidants due to carboxyl groups which can destroy free radicals, and are also helpful in cancer diseases due to their degenerative activity [23, 24, 25, 26]. In the near future, nanotechnology will find its application in the production of cosmetic packaging [10]. In the cosmetic industry, copper nanoparticles are used

as fungicidals, nanoplatinum ions have rejuvenating and regenerating effects on the skin cells, mainly age spots and hepatic spots [11]. Gold ions in the form of nano regenerate and stimulate the skin cells.

They stimulate the production of collagen and renewal of skin tissue. Applied externally they reduce wrinkles, detoxify the body, treat abscesses, lichenes, chronic rashes and acne. They have anti-inflammatory properties, and are used in burns treatment [13].

The products in which nanoparticles occur are more effective because active ingredients are delivered to their target place. An additional advantage is their radioprotective effect on the skin and antioxidant activity [13].

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