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Abstract

Nanofibers form the broadest class of nanomaterials due to their unique properties. High surface-area-to-volume ratios, low diameters, high strength values, low basis weights, high porosities, and small pore sizes make them good candidates for numerous applications. Cosmetics are one of these important application areas. Excellent interaction with environment (e.g., skin or damaged tissue), increased loading capacity for agents, high liquid absorption capacities, high oxygen, and water vapor permeability values are provided by characteristic properties of nanofibers. They are used as therapeutics, facial masks, skin care, and renewal products. This chapter will provide an overview of nanofibers in cosmetics. A brief history of cosmetics, different types of nanomaterials used in cosmetics, nanofiber properties, and production methods are described in this chapter. Novel applications of nanofibers in cosmetics are also mentioned.

Keywords: nanofibers, cosmetics, facial mask, skin care

1. Introduction

To be admired and look beautiful are two basic phenomena that exist in human nature. Seeming beautiful and clear and feeling admiration increase people’s self-confidence and make them satisfied in terms of psychology. Besides seeming good and well-groomed, requirement for personal care increases the popularity of usage of cosmetics. The use of cosmetics is based on the ancient age. Archaeological excavations have proved that cosmetics have been commonly used in ancient Egypt. Dyes and paints that are used for coloring the skin and oils and perfumes that are used for personal hygiene were the earliest cosmetic products [1]. Although cosmetics were used in ancient age, they have become widespread in the 1900s and during the World War II and more conscious approaches for cosmetics usage have begun to be shown [2,
As in every field, with the developments in cosmetics, qualities of cosmetic products used nowadays are enhanced and diversities of these products are increased. Especially, insertion of nanomaterials (nanofibers, nanoparticles, nanoliposomes, nanopigments, etc.) into the structures of cosmetics has given a new point of view to the cosmetic sector [4, 5].

Ancient Greek word “nanos” that means dwarf is used to describe the physical magnitudes in orders of $10^{-9}$. Nanomaterials can be defined as materials having controllable sizes of 100 nm or less. Nanomaterials with enhanced properties are obtained by the reason of the fact that sizes at nano scales affect the structural, mechanical, thermal, thermo-dynamical, kinetical, and electrical properties of materials [6]. Since the discovery of these nanomaterials, rapidly increasing interest has been shown by the academic world and this has led to the production of various nanomaterials for diverse sets of applications. One of these application areas is cosmetics.

The usage of nanomaterials in cosmetics has continued for 40 years and has become popular since 1990s. The first usage of nanomaterials in cosmetics has been seen in moisturizers with liposomes. Nowadays, nanomaterials are widely used in sunscreen creams, anti-aging creams, hair products (such as anti-hairloss, anti-hairgraying, etc.), facial masks, and toothpastes [4, 5]. Also, personal care cosmetic products such as soap, shampoo, bronzer, moisturizer, foundation, and lip sticks are other examples of cosmetics that uses nanostructured materials [7, 8]. Besides personal care, researchers have been focusing on skin health care during the last decades. Skin wound healing, drug/agent delivery to skin for anti-wrinkle, and anti-aging purposes, and artificial skin applications are some challenging nanomaterial applications in cosmetics.

2. Nanomaterials in cosmetics

An engineered nanomaterial is defined as a material that is intentionally produced as having at least one dimension between the range of 1 and 100 nm [9]. Nanomaterials’ molecular structure and advanced interactions with the environment are the two important factors that affect preference of nanomaterials in cosmetics [10]. The nanomaterials used in cosmetics can be classified as nanoemulsions, nanoliposomes, nanopigments, and nanofibers. These are all used in sunscreens, skin creams, hair products, and oral hygiene products [11].

2.1. Nanoemulsions

Nanoemulsions are defined as transparent or translucent liquid dispersion systems which are thermodynamically or kinetically stable. They contain nanometric sized droplets of water and oil. A surfactant is also found in the dispersion. There are three types of nanoemulsions depending on the composition: oil in water nanoemulsion (continuous aqueous phase where oil droplets are dispersed in), water in oil nanoemulsion (continuous oil phase where water droplets are dispersed in), and bicontinuous nanoemulsion (system where oil and water are interdispersed in) [12–16]. High pressure homogenization, microfluidization, phase inversion, sonication, ultrasonic system, and jet disperser methods are some methods that are used for the preparations of nanoemulsions [14, 15]. Physicochemical characterization of nanoe-
emulsions can be performed by particle size analysis, rheological measurements, refractive index, and surface tension tests [14].

There are some advantages of nanoemulsions than the other types of emulsions, such as macro- and microemulsions. The amount of surfactant is lower in nanoemulsions when compared to microemulsions [17]. The advantages in terms of optical, tactile, and texture properties make nanoemulsions attractive in cosmetics. The problems like inherent creaming, flocculation, coalescence, and sedimentation that occur in macroemulsions and even in microemulsions have not been met in nanoemulsions due to their small droplet sizes which enhance transparent view and fluid properties [15, 18–20]. Reducing the sizes of emulsions to nanometers provides an increase in the content of nourishing oil, and by this means, the transparency and the lightness of the formula are preserved. Also, allowing fragilely transport of the active ingredient (like vitamins) to the skin by means of higher surface area is another advantage [11]. Properties such as freshness, purity, simplicity, and rapid penetration make nanoemulsions valuable for the cosmetic industry [12, 18, 21–23].

Sun care products, moisturizing and anti-aging creams, conditioners, and lotions are some of the examples of nanoemulsions. Another attractive example of oil-in-water form of nanoemulsions is polyethylene glycol emulsifier-free emulsions that have low-viscosity. With the advent of its moisturizing effect and low viscosity oil in water emulsions, it is used in emulsion-based wet wipes for baby-care and make-up removal. In addition to these products, nanoemulsions have potentials for personal hair products. For dry hairs, extended effect provided by cationic nanoemulsions usage makes hair gain less brittle, nongreasy, and shiny [12, 15, 24, 25]. Also, coenzyme encapsulated nanoemulsions enhance the collagen synthesis of fibroblasts. Cell culture studies revealed that there was an increase in the secretion of collagen when studied with coenzyme added nanoemulsion [26].

2.2. Nanoliposomes

Nanoliposome, as a term, means nanoscaled bilayered lipid vesicles or liposomes in the low nanometer size range. Phospholipid molecules of components combine in an aqueous solution to give a colloidal structure. This structure preserves its nanometric size during storage and application period in virtue of polar and nonpolar regions of bilayer forming molecules.

Nanoliposomes have the same physical, structural, and thermodynamical properties and also have the same way of formation with liposomes. Formation of both depends on the hydrophilic–hydrophobic interaction between phospholipids and water molecules [27–29]. There are various methods to produce nanoliposomes. High-pressure homogenization is one of the techniques and is used to produce liposomes ranging from 20 to 50 nm in size. Some of the other methods for producing nanoliposomes are sonication technique, extrusion method, microfluidization, heating method, and Mozafari method. Characterization of nanoliposomes may be performed by electron microscopy, radiotracers, fluorescence quenching, ultrasonic absorption, electron spin resonance spectroscopy, and nuclear magnetic resonance spectroscopy. Visual appearance, size distribution, stability, zeta potential, lamellarity, and entrapment efficiency may be investigated [30, 31].
Encapsulation and delivery of bioactive agents can be achieved by nanoliposomes. These can be used in cosmetics, nutraceuticals, and pharmaceuticals. In the cosmetic sector, nanoliposomes are important because of their nanosized structure. They do not clog skin pores and allow penetration of air and water-soluble materials, while the many types of cosmetic products cause accumulation of oil layer on the skin and block passing of air, water, vitamin, etc. through the skin. Benefiting from these features, some trademarks claim that they produce cosmetics with immediate lifting effect. As a result, nanoliposomes give wrinkleless effect to the skin appearance [31–33].

2.3. Nanopigments

Dispersions of organic and inorganic nanopigments have been used in various applications such as printing, paints, coatings, cosmetics, and color filter arrays for the display industry. Nanopigments or pigment nanoparticles which differ from the bulk materials are functional nanomaterials that are used in the cosmetics industry with a gradually broadening trend. The nanoinorganic pigments having particle sizes less than 100 nm are considered as an insoluble and chemically and physically inert into the substrate or binders [34–36].

Nanopigments have the advantage of consisting ultrasmall particles, and certainly, the dispersion of ultrasmall particles in solvents is easier than the larger ones. Also, their small shape enables more stable dispersion because the gravity can be ignored with regard to the other forces like van der Waals forces. Another advantage is the ability of forming closed packed films. Capillary force of small particles is greater than that of large particles [34].

Nanopigments already exist in our natural environment. Titanium dioxide (TiO₂) and zinc oxide (ZnO) are the well-known examples of nanopigments. Since they have unique capacity to reflect UV light, they are commonly used in sunscreens. They protect human skin against damages like skin cancer arising from UV radiation [37]. Other examples in the cosmetic market are firming lotions, bronzers, exfoliant scrubs, eye liners, hair coloring products, and styling gels [38–40]. Nanoaluminum oxide having the feature of diffusing the light with concealers and mineral foundations provide smooth effect to wrinkled areas on the face. Mica-based pigments are also used in cosmetics since they give pearlescent effect [35, 36, 39].

2.4. Nanofibers

Nanofibers are the last and the largest of nanomaterials used in cosmetics and are discussed in detail in Section 3.

3. Nanofibers: definition and properties

Fiber is defined as a unit of matter characterized by length, fineness, and high ratio of length to thickness by the Textile Institute [41]. Nanofibers are characterized as nanomaterials that have at least one dimension, that is, 100 nm or less, according to the definition of American National Science Foundation [42, 43]. Nanofibers are classified as one-dimensional (1D)
nanomaterials (having a degree of freedom in one direction). Apart from the definition in textiles, nanofibers are defined as fibers that have a minimum ratio of length to thickness of 1000:1 [44].

Properties of nanofibers can be specified as having low unit length (diameter), high surface-area-to-volume ratio, high strength value, low basis weight, high porosity, and small pore size [45–48]. These make them indispensable in numerous applications.

Increasing the number of fibers in a unit volume can be achieved by decreasing the diameters of fibers and by migrating atoms from the bulk to the surface. This leads to an increase in surface-area-to-volume ratio, and hence the enhanced liquid absorption capacities and increased retention levels of functional groups, ions, particulates, or agents are obtained. High contact surface area between nanofibers and skin provides delivery of cosmetic agents to the deeper skin parts. All these mean advancement in the activities of materials including nanofibers instead of micro ones (Figure 1).

![Figure 1. An exaggerated drawing of migration of atoms from bulk to surface and variation of properties with size.](http://dx.doi.org/10.5772/64172)

The other properties enhanced by size reduction are the oxygen and water vapor permeability capabilities. According to high porosities and low pore diameters observed in nanofiber mats, breathable cosmetics can be successfully produced. This gains importance in terms of dermocosmetics that comprises cleaners, moisturers, and photoprotectors [49].

Mechanical strength of nanofibers is significant in terms of usage as artificial skin mats [50]. Since the mechanical properties of polymers are determined by molecular structure, weight, and orientation, polymer nanofibers that can be produced as highly molecularly oriented by fiber production methods serve as good templates in artificial skin applications. Low basis weight of nanofiber mats is the other great property.
4. Production methods of nanofibers

Nanofibers have been designed by choosing suitable polymers, convenient additives, and proper production methods to meet the requirements of their specific application area. Nanofibers are produced by lots of methods such as self-assembly, drawing, meltblowing, template synthesis, phase separation, melt spinning, centrifugal spinning, and electrospinning [51]. Flash spinning is a modified spunbond method and is also considered as one of the nanofiber production methods in some references [52]. The method is based on the formation of fibrillar formed filaments by extrusion through a spinnnet and removal of solvent. But there is a lowest limit of about 1 μm for nanofiber diameters [53].

Although nanofibers can be achieved by the abovementioned methods, electrospinning is the unique method for the production of nanofibers in cosmetics. All the methods are described briefly except electrospinning, which is discussed elaborately because of its prevalence.

All the methods require sensitiveness at different levels due to the complexity of the process. Since the production is made in nanometer ranges, it should be avoided from atmospheric contaminations. If a visible threshold of about 40 μm is considered, the importance of clean process environment will be well understood.

4.1. Self-assembly

Self-assembly is the only nanofiber production method that benefit from bottom-up approach [54]. The term “self” corresponds to formation of molecules and molecular chains by atoms, finally forming fibers by molecular chains with minimum external effect [55]. The mechanism is based on formation of up structures (nanoscaled fibers) from bottom structures (molecules). The drawbacks of the method are complication of process and uncontrollable fiber diameters [56]. Leibmann et al. have found that self-assembled spider silk nanofibers and microbeads have potentials to be used in cosmetics and pharma [57].

4.2. Drawing

Drawing of individual nanofibers is achieved by a micromanipulator probe taking a little amount of polymer from the viscoelastic polymer solution droplet placed on a flat surface. Probe takes this little amount of polymer on and then draws it at a slow constant rate. By the contact of probe onto the flat surface at a distance adequate for fiber length, individual fibers are succeeded. Drawing rate and solvent evaporation rate are the important process parameters [56, 58, 59]. Polycaprolactone, polyethylene oxide, hyaluronic acid, fish gelatin blend, and polymethylmethacrylate are the biopolymer nanofibers formed by the drawing method [60], and in addition these, polymer nanofibers can be used as skin tissue scaffolds or skin wound healers.

4.3. Meltblowing

High flow rate of hot air is contacted with polymer extruding out of a capillary tip. Nanofibers are formed at a very short time [61]. The viscosity of the polymer melt should allow
sufficient thinning of nanofibers in this process [62]. In this method, nanofibers of approx. 250 nm diameter can be obtained with low cost by using thermoplastic polymers [63]. The most common applications of meltblown nanofiber mats are filtering applications [64, 65]. Wet wipes constitute the other class of applications [66, 67]. Also, a pack of cosmetic facial mask including a meltblown fiber mat layer was presented by Choi and Lee [68].

4.4. Template synthesis

As it is understood from the name of the method, templates are used for the production of nanofibers. Electrochemical, chemical, sol-gel, and chemical vapor deposition are some types of template synthesis [69]. Fiber diameters are determined by pore sizes of the templates. Since the process needs preliminary preparation (e.g., preparation of metal oxide nanoporous membranes), it is time consuming. Tao and Desai have pointed out the usage of biodegradable polymers for the production of template synthesized nanofibers for tissue engineering applications [70].

4.5. Phase separation

Basic principle of the phase separation is the formation of polymer-rich and polymer-poor phases and formation of nanofibrous structure after the removal of polymer-poor phase. A 3D fibrous structure is obtained instead of mats composed of individual fibers [56, 71].

Type of solvent and polymer, concentration of polymer solution, and temperature are the key parameters that affect the process [71]. Although there are limitations about the polymers that can be used in this method, there is an advantage of adjusting the mechanical properties by changing polymer concentration. Minimum equipment requirement is the other advantage [56, 72].

4.6. Melt spinning

In this continuous process, melt is drawn first and then fiber is wound with a faster rate than in extrusion [73]. Bicomponent spinning is a modified melt spinning method in which unconventional spinnerets are used. As it is obvious from the name of the method, two components are extruded through the spinneret, and then one component is removed and the other one remains [74]. Different spinneret designs may be used in the production. Islands in the sea model is the most used one [75]. Fibers approximately with diameters of 300 nm may be obtained by drawing 1 denier (g/9000 m) fibers from the island in the sea type spinneret [52].

4.7. Centrifugal spinning

Centrifugal spinning method is proposed as a method that exceeds the limitations of other nanofiber production methods such as available materials, production rate, safety, and cost [76]. A polymer melt is fed toward a spinning head (with a rotational speed of approx. 3000 rpm) which forms the centrifugal force that is required for sufficient attenuation [77]. There is an assistance of high velocity air during the transition of nanosize [76]. Centrifugally spun
biopolymer nanofibers were proposed as successful skin grafts with increased cell attachment and proliferation [78].

4.8. Electrospinning

Electrospinning is a simple peerless method that individual nanofibers can be formed continuously. It allows production of functionality added nanofibers from polymer solutions/melts to be used in various applications. Since electrospinning equipment is cheap and the process is simple, it is attractive for lots of researchers to produce nanofiber webs from a wide range of polymers.

Figure 2. Schematic figure of (a) a coaxial needle and (b) an equipment with a rotating drum collector.

Basis of static electricity were laid by ancient Greeks. Thales of Miletus (630–550 BC) was the one who realized the force created by amber (electron) on objects. The first written evidence has been left by Theophrastus (374–287 BC) [79, 80]. William Gilbert has used an amber rod for drawing water droplets [80, 81]. From the 1700s lots of researchers investigated the behavior of droplets under electrostatic forces, electrospaying, stability of drawn jet, cone formation, and so on [51]. Producing silk-like synthetic fibers was an important topic in the 1900s. In 1934, Formhals took 11 patents about the subject. His mischance was the invention of polyamide
with a higher output than proposed in Formhals’ methods [47]. As the academic interest increased by the time, the method was developed by modifications in feeding and collecting units as seen in Figure 2a and b, respectively. Coaxial needle provides feeding of two different polymers or encapsulation of agents, drugs, or other bioactive materials inside the shell polymer acting as a carrier. Rotating drum collectors develop the fiber structure, provide molecular orientation, and make electrospinning easy with high angular velocity.

The principle of electrospinning is drawing of nanofibers under the electrostatic forces created with the usage of high voltage power supply and grounding placed on needle and collector, respectively [82–85]. The steps encountered in the process may be classified into six groups: the first one is the charging of polymer solution/melt causing a deformation on the droplet at the tip and the formation of cone [86, 87]. The second one is the generation of jet by increasing charging. This causes a deformation in jet [86–88]. At the third stage, the straight jet segment elongates [89, 90]. Deformation of straight jet segment, creation of instability, and continuation of elongation compose the fourth step [91, 92]. In the fifth step, solidification of nanofibers takes place by evaporation of solvent or cooling [87, 93]. And finally, fibers showing buckling behaviors are collected on the collector [94].

As one can understand from the six basic steps of electrospinning, the rate of feeding, electric field force acting on polymer solution/melt, and the flight distance of polymer jet are the key parameters of electrospinning process. It is known that none of the parameters can be evaluated independently from each other. In other words, there are optimum electrospinning parameters for every polymer solvent system or polymer melt. Since the adjustments of these parameters are easy, it can be said that the method still maintains its position at the focus of academic interest.
Producing nanofibers quite easily from various polymers makes electrospinning and electro-spun products indispensable for a diverse set of applications. The electrospun nanofiber mats, as shown in Figure 3, may be used in drug delivery systems, therapeutics, and body care supplements [95].

5. Applications of nanofibers in cosmetics

Nanofibers take the advantage of their unique properties and have extensive usage in cosmetics, tissue engineering, biomedical, filtering, composites, protective clothing, electrical and optical applications, sensors, and agriculture [80, 96]. Since nanotechnology allows production of value-added products, cosmetics produced by nanotechnological methods have attracted attention from every area. With the aid of nanofiber production methods, especially by electrospinning, mats with controllable pore sizes and fiber diameters can be obtained. Also, the novel approaches that have been shown to cosmetics led to consumption of more conscious cosmetic products including therapeutic products and products for skin health and renewal (such as facial masks for skin cleansing, skin healing, and skin therapy) [95, 97]. All of the products mentioned above can be produced by using nanofibers. Applications of nanofibers in cosmetics are described below.

5.1. Facial masks and skin cleansings

Fathi-Azarbayjani et al. have presented an antioxidant and anti-wrinkle nanofiber face mask. They added ascorbic acid, retionic acid, collagen, and gold nanoparticles to the electrospinning solution and directly spun the fibers. In order to avoid from instability problems of prewetted facial masks, they have designed a mask that will be wetted just before the application. They indicated that wetting of masks will provide the release of agents from nanofibrous mats and ensure high skin penetration due to the high surface area of nanofibers. Thus, they developed healthy appearance of skin [98]. Smith et al. have a patent related to skin care mask. This mask is composed of nanofibers and can be used as a cleansing product for overaccumulated oil on skin [99]. Also, skin revitalizing factors can also be impregnated to nanofiber-based masks [95]. Kim designed a water soluble nanofiber layer for removal of cosmetic ingredients. He argued that dissolution of nanofiber layer by water maximized adhesion to the skin [100].

5.2. Skin health and renewal products

Researcher groups have attempted to electrospin nanofibers with various agents and investigate the effects on skin health. One of them produced cellulose acetate nanofibers by loading vitamin A and E to the spinning solution. They have searched the dermal therapeutic effect of vitamin loaded nanofiber mats as carriers. They compared the release of vitamins from the nanofiber mats and cast films and have not come across with a burst release in nanofibers as seen in cast films [101].
Another study including the loading of vitamin E to silk fibroin nanofibers was conducted in 2013. The researchers have argued that the mats presented in the study can be used as personal skin care products since they enhance the survival of the L929 fibroblast cells during in vitro tests [102].

5.3. Skin wound dressings and drug delivery products

Delivery of drugs to the skin can be considered in cosmetic applications, especially in dermocosmetics. Sufficient delivery results were observed due to the higher surface area of nanofibers [103]. A researcher group has prepared electrospun chitosan-based nanofiber mats with Garcinia mangostana extracts. The agent has made the nanofiber mats antioxidant and antibacterial. According to the in vivo wound healing test results, acceleration in wound healing has been observed. They stated that these extract loaded chitosan nanofiber mats were good candidates for dermal healing mats [104]. Charernsriwilaiwat et al. were the ones trying to load lysozyme on chitosan nanofibers. Enhancement in wound healing was observed in in vivo tests of Male Wistar rats [105]. Vargas et al. revealed that electrospun hyperbranched polyglycerol nanofibers involving Calendula officinalis extract were suitable for wound dressing materials. They investigated the water vapor permeability, cytotoxicity, and skin irritation values and found that these nanofiber mats were proper for wound healing [106].

Silver nanoparticles are known as antimicrobial agents. Silver nanoparticles damage bacteria, virus, and fungi, and so they can be used as wound healing agents [107]. Nguyen et al. produced silver nanoparticles loaded with PVA electrospun fiber mats for wound healing. High antibacterial activities against S. aureus and E. coli were observed that is important for rapid wound healing [108]. Rujitanaroj et al. produced gelatin nanofibers with silver nanoparticles. They recommended that these mats can be used as dressing materials for burn wounds [109].

Epidermal growth factor added silk fibroin nanofiber mats were produced by electrospinning technique to improve wound healing process [110]. Also, Han et al. investigated nanofiber-based dressing from poly(3-hydroxybutyrate-co-3-hydroxyvalerate) polymer. They found that wound healing was supported at early stages by providing proper moist and mechanical support to the wound environment [111]. Poly(L-lactic acid) nanofibers were obtained in another study as skin tissue scaffolds. The success of the product was associated to the similarity of the structure of nanofibers to the extra cellular matrix of the skin [112].

6. Conclusions

Nanofibers have great potentials for use in cosmetics. Advances in fiber production technologies allow the design of new products for versatile usage in cosmetic applications. Increase in the awareness of usage of cosmetics in skin care as well as in therapy and healing directs researchers to conduct more research this field. It seems that nanofibers will continue to attract attention in this specific application area for many years.
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