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Chapter

Skin Care Nanocosmetics

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Abstract

The improvement of stability, solubility, spreadability and skin penetration of cosmetics as well as the reduction of oxidation may be achieved by nanocarriers. In that regard, many cosmetic industries have launched nanocosmetics due to their performance improvement. Sunscreens, moisturizers and anti-aging products based on nanotechnology are available worldwide. In addition, vegetable extracts loaded into nanocarriers have also been employed as a strategy to increase their skin penetration. In this chapter, the main contributions of polymeric nanocarriers, lipid nanocarriers and vesicular nanocarriers to skin care cosmetics were approached.

Keywords: nanocosmetics, polymeric carriers, lipid carriers, vesicular carriers, skin

1. Introduction

Since the beginning of human civilization, there is a search for beauty and well-being [1]. Currently, people are willing to perform different procedures to prevent skin aging. This trend is reflected in an increased number of skin care products over the years [2]. Along with population aging and increased cosmetic consumption, innovative cosmetics have been targeted by cosmetic industries to develop improved performance products [3]. In this context, nanocosmetics are reported since 1986 [4] to improve formulations efficacy and stability [4, 5].

Several cosmetics based on nanotechnology are available for skin, hair and skin appendages. Among these, skin care nanocosmetics account for most commercial products, with emphasis on those with anti-aging, moisturizing, anti-wrinkle, anti-oxidant and sunscreen properties [6]. Mainly for women, anti-aging and anti-wrinkle claims products are highlighted [7].

This chapter will address the state of art and the most recent contributions of nanocosmetics for skin care, with emphasis on the most employed nanocarriers. Hence, polymeric carriers (i.e., nanocapsules and nanospheres), lipid carriers (i.e., solid lipid nanoparticles, nanostructured lipid carriers and nanoemulsions) and vesicular carriers (i.e., liposomes, transfersomes and niosomes) will be approached.

2. Cosmetics based on polymeric nanocarriers

Polymeric nanoparticles are bioactive carrier systems formed essentially by polymers of synthetic or natural origin. Among these, the most widely used are poly (lactic acid) (PLA), poly (d,l-lactic acid-co-glycolic acid) (PLGA), poly(alkyl cyanoacrylate) (PACA), and poly (ϵ -caprolactone) (PCL) (synthetic polymers) and gelatin, albumin and chitosan (natural polymers) [8]. These nanoparticles have been investigated to increase the stability of cosmetic actives, control their release, increase cutaneous penetration, and avoid incompatibilities between formulation ingredients [4].

These systems can be divided into nanocapsules and nanospheres (**Figure 1**), which differ according to their composition and structural organization. Nanocapsules (**Figure 1b**) consist of a polymeric shell arranged around an oily core, and the active ingredient may be dissolved in this core and/or adsorbed to the polymeric wall. On the other hand, nanospheres (**Figure 1a**), which do not have oil in their composition, are formed by a polymeric matrix, where active ingredient is uniformly dispersed or solubilized inside this matrix and may be retained or adsorbed [9].

Nanocapsules have been extensively investigated as vehicles for chemicals sunscreen such as octyl methoxycinnamate, octyl salicylate, and benzophenone-3 [10, 11]. From this perspective, there are reports of the development of polymeric nanocapsules coated with chitosan, which is a cationic, biocompatible, bioadhesive and FDA-approved polymer, to increase the skin adhesion and the photoprotective effect of sunscreen [12]. Also, these nanoparticles are able to form a protective film on the skin surface and control the penetration and permeation of the encapsulated substances [13]. In that regard, *ex vivo* permeation studies performed on porcine ear skin have decreased benzophenone-3 permeation [14]. Another promising application of polymeric nanocapsules in skin care is the increased anti-acne activity of tea tree oil [15].

As to nanospheres, they are used to encapsulate fragrances and vitamins [16]. In this sense, there are reports that fragrances encapsulated in nanospheres remained on the skin after a long period of application. In addition, PLGA nanospheres containing ascorbyl tetraisopalmitate had a higher skin deposition [17]. Apart from that, chitosan content affected the encapsulation efficiency of alpha-arbutin loaded in chitosan nanoparticles. Also, the mode of incorporation of the drug also influenced the encapsulation efficiency. Therefore, formulation optimization is essential to obtain suitable physicochemical features and an improvement of alpha-arbutin-loaded chitosan nanoparticles on melasma treatment [18].

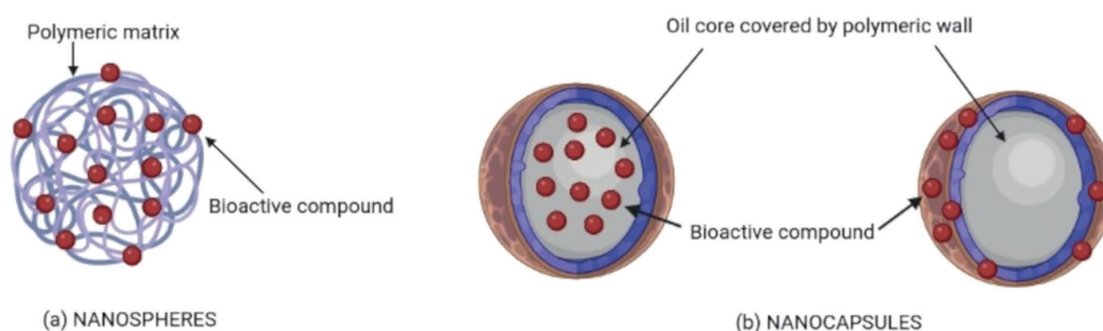


Figure 1.
Nanospheres and nanocapsule structure [9].

Regarding nanospheres' application to photoprotection, gelatin nanoparticles were applied for encapsulation of natural compounds, such as rutin [19] and *Baccharis antioquiensis* extract [20]. In both reports, there was improved photostability and increased photoprotection [19, 20]. **Table 1** summarizes the main results of polymeric nanoparticles and other nanocarriers applied to cosmetics.

3. Cosmetics based on lipid nanocarriers

Lipid-based nanocarriers are composed of a lipid core, where they encapsulate one or more biologically active substances. In general, they can provide less toxicity, in addition to several other favorable attributes, such as increased penetration into the skin, possibility of sustained release and protection of actives against degradation, among others [3, 36]. Lipid-based nanocarriers comprise solid lipid nanoparticles (SLNs), nanoemulsions (NE) and nanostructured lipid carriers (NLCs). Lipid-based nanocarriers are increasingly present in the cosmetics market in skincare products, due to their beneficial properties for the skin [37]. They are able to effectively solubilize and deliver hydrophobic active ingredients to the skin, resulting in greater efficacy of cosmetic products [36].

SLNs comprise the first generation of lipid-based nanocarriers, being introduced in the last decade of the twentieth century. SLNs are constituted of a solid lipid core stabilized by a surfactant layer, being able to successfully deliver lipophilic actives to the upper skin layers [38, 39]. In practical terms, SLNs offer the possibility of large-scale production, not relying on organic solvents for their preparation, and rigid morphology, which increase their stability [39, 40]. SLNs are considered the most

| Nanocarriers | | Cosmetic ingredient | Main outcomes | Cosmetic use | Ref. |
|------------------------|-------------------------------|----------------------------|---------------------------------------|--------------|------|
| Polymeric nanocarriers | Nanocapsules | BP-3* | Decreased permeation | Sunscreen | [14] |
| | | bp-3* | Increased skin adhesion | Sunscreen | [12] |
| | | | Increased photoprotection | | |
| | | Tea tree oil | Increased anti-acne activity | Anti-acne | [15] |
| | Nanospheres | Rutin | Increased photostability | Sunscreen | [19] |
| | | EHDP* | Increased sunscreen protection factor | Antioxidant | |
| EHMC* | | | | | |
| | BMDBM* | | | | |
| | | VC-IP* | Increased permeation | Antioxidant | [17] |
| Lipid nanocarriers | Solid lipid nanoparticles | Caffeine | Faster skin permeation | Anti-aging | [21] |
| | | Oxybenzone | Increased skin hydration | Sunscreen | [22] |
| | | | Increased photoprotection | | |
| | Nanostructured lipid carriers | Coenzyme Q10 | Improved skin penetration | Anti-aging | [23] |
| | | | | Antioxidant | |
| | | NDAG* | Prolonged release | Antioxidant | [24] |
| | | Higher antioxidant ability | | | |
| | | Carrot extract | Increased skin hydration | Antioxidant | [25] |
| | | Marigold extract | Increased skin elasticity | | |

| Nanocarriers | | Cosmetic ingredient | Main outcomes | Cosmetic use | Ref. |
|----------------------------------|---------------|--------------------------------|-----------------------------------------------------------|------------------------------|------|
| Vesicular nanocarriers | Liposomes | Vitamin C | Higher photostability | Antioxidant | [26] |
| | | <i>Lactobacillus rhamnosus</i> | Lower cytotoxicity | Antioxidant Antimicrobial | [27] |
| | | 4nBR* RSV* | Decreased melasma index | Hyperpigmentation | [28] |
| | | Cysteamine | Lower oxidation | Hyperpigmentation | [29] |
| | | Ascorbic acid | Increased skin permeation Increased collagen synthesis | Antioxidant Anti-aging | [30] |
| | | <i>Coffea arabica</i> extract | Higher stability for liposomes /polyhydroxy butyrate | Antioxidant Sunscreen | [31] |
| | Aspasomes | MAP* | Higher skin permeation and decreased MASI score | Hyperpigmentation | [32] |
| | Niosomes | Melatonin | Higher skin penetration | Antioxidant Sunscreen | [33] |
| | | EHMC* | Lower skin penetration | | |
| | Transfersomes | RSV* | Higher stability | Antioxidant | [34] |
| <i>Myrciaria jaboticaba</i> peel | | Higher stability | Antioxidant | [35] | |

*BP-3: benzophenone-3, EHDP: ethylhexyl dimethyl PABA, EHMC: ethylhexyl methoxycinnamate, BMDDBM: methoxydibenzoylmethane, VC-IP: ascorbyl tetraisopalmitate, 4nBR: 4-n-butylresorcinol, RSV: resveratrol, NDAG: naringenin; kaempferol nordihydroguaiaretic acid, MAP: Magnesium ascorbyl phosphate.

Table 1.
Main outcomes of nanocarriers for cosmetic application.

used lipid nanoparticles in the cosmetic field [36]. SLNs stand out in terms of stability and long-term storage [41].

The advantages of SLNs include (i) possibility of using biodegradable physiological low-toxicity lipids with low toxicity and (ii) ability to form a single-layer film with a hydrophobic character, which provides an occlusive effect on the skin, preventing transepidermal water loss [22]. The occlusion capacity also increases skin elasticity and flexibility, which makes SLN and NLC useful for anti-aging products [22]. In that regard, caffeine-loaded SLN had a faster skin permeation for over 24 hours due to the occlusive effect provided by SLN [21]. The addition of caffeine into skin care products prevents UV-induced photoaging due to its ability to reduce blood flow and antioxidant effects [42].

However, SLNs have shown some drawbacks through the decades: the low entrapment capacity [43], possibility of sudden burst release [44] and the tendency of crystallization of solid lipids [40]. In that context, nanostructured lipid carriers have been developed (NLCs) as a second generation of lipid NPs. NLCs are an advancement to SLNs, bearing a peculiar core composition: a blend of solid lipid and a liquid lipid (e.g. an oil) [40]. The mixture of solid and liquid lipids in NLCs improves stability in comparison to SLNs [3].

Regarding topical application, NLCs provide skin occlusion, skin hydration and sun photoprotection [39]. They are versatile structures allowing the delivery of antioxidants, moisturizers, sunscreens and other bioactive compounds [36]. Similar to SNPs, NLCs improve skin penetration. Coenzyme-Q10 NLC had a higher skin penetration in regards to nanoemulsions and would be an interesting approach to

improve antioxidant activity in deeper layers of the skin [23]. Moreover, natural antioxidant compounds encapsulated in NLCs had a prolonged release profile and physicochemical stability for at least 30 days. Therefore, NLCs are effective skin-delivery vehicles for natural antioxidants [24]. In other reports, hydrogel containing vegetable compounds loaded with NLC scavenged free radicals and provided an increase in skin hydration and skin elasticity [25].

The advantage of developing skincare products using both SLNs and NLCs lies in improving the skin absorption of lipid bioactive substances, as nanocarriers increase the cosmetic ingredients solubility. Moreover, their reduced size allows a higher possibility of skin penetration. In addition, once applied to the skin, the nanolipid structures can increase occlusion, which also provides an increase in skin barrier function [3, 36].

Nanoemulsions (NEs) are thermodynamically unstable colloidal systems composed of an oil and aqueous phase and emulsifiers that form lipid-core nanoparticles, with a diameter ranging from 20 to 500 nm [3]. Among the advantages of NE, one can highlight: (i) NEs feature a transparent or translucent appearance; (ii) desired skincare product properties such as low viscosity, great spreadability and pleasant texture; and (iii) enhanced skin hydration [45].

Also, NE can be found as a base for various skincare and cosmetic products, such as deodorants, shampoos, sunscreens, conditioners, and skin and hair serums [46, 47]. NE-based products are among the most popular and commercially available. For instance, Kemira nano-gel is a nanoemulsion-based patented cosmetics system meant to promote skin smoothness [47, 48]. Other commercial cosmetics bearing nanoemulsions are available for skin hydration and skin anti-aging [49].

Besides, NE is acceptable in cosmetics because they are light, transparent and less prone to creaming, sedimentation, flocculation, or coalescence regarding macroemulsions [50]. Further, oil-in-water NEs play an important role in cosmetics as they are fundamental in body lotions, skin creams and sunscreens products. Yet, a recent but fast-growing field of application is wet wipes. It is highly attractive in the growing market for baby care and make-up removal products [51].

4. Cosmetics based on vesicular nanocarriers

Liposomes have been reported as cosmetics carriers since the late 1970s [52] for several skin applications including hydration, anti-aging and sunscreen [6]. They are formed by lipid lamellae and an aqueous core [53] (**Figure 2**), and due to the presence of phospholipids, liposomes have limited stability [5]. Additionally, liposomes usually provide a more superficial skin release, at the stratum corneum level. Hence, other vesicular carriers (**Figure 2**) were developed aiming to obtain more stable formulations and to provide a deeper skin release into the skin [53]. In that regard, transfersomes and niosomes were developed [54]. Transfersomes are vesicular carriers containing phospholipids and an edge activator. Diversely, niosomes are vesicular systems bearing non-ionic surfactants instead of phospholipids [54].

The approach of using plant extracts loaded into vesicular systems [35, 55] and natural-ingredients have been explored as new cosmetics formulations [27, 56, 57]. Moreover, as microbiome is important to skin health and its imbalance is related to disease occurrence, probiotics are also addressed as skin care products [58]. In this sense, probiotics loaded in liposomes reduced the unpleasant odor, an interesting feature to increase adherence to product use, which consequently may contribute to skin health maintenance [27].

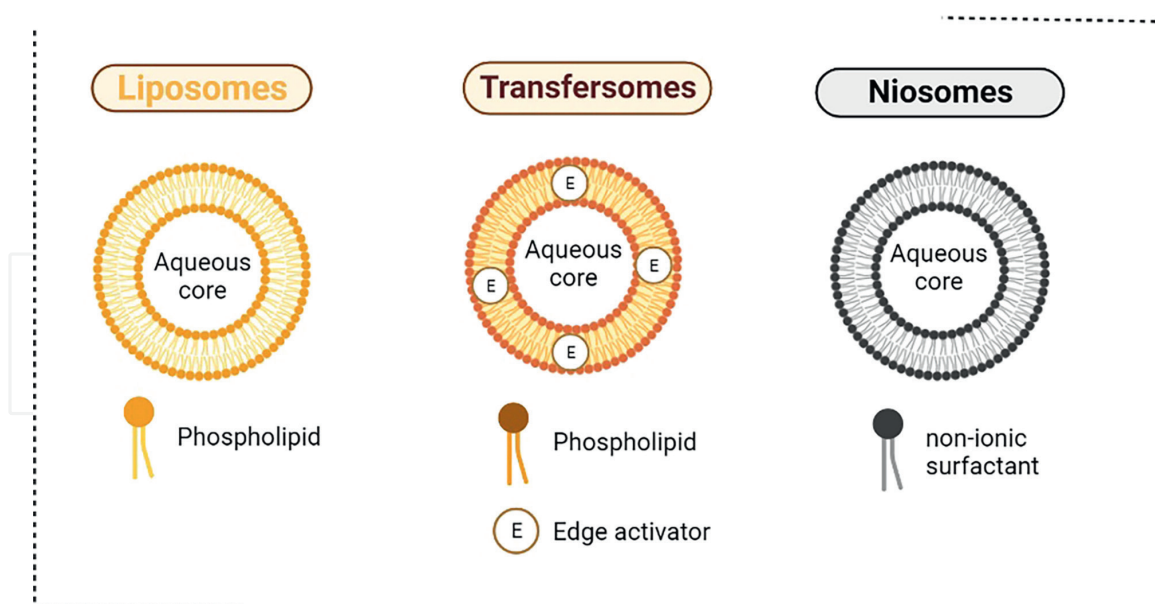


Figure 2.
Vesicular carriers: Liposomes, transfersomes and niosomes [53, 54].

Regarding skin permeability, deformable liposomes bearing taxifolin or taxifolin tetraoctanoate showed a greater skin permeation compared to non-deformable liposomes [57]. Likewise, aspasomes, lipid vesicles containing magnesium ascorbyl palmitate, had a greater skin permeation. The use of a more stable vitamin C derivative with a more lipophilic nature is an approach to improve skin delivery of vitamin C [32]. Furthermore, octyl methoxycinnamate Pickering emulsions containing melatonin-loaded niosomes provided a deeper penetration for melatonin while also providing a low skin penetration of octyl methoxycinnamate [33]. As melatonin is an antioxidant, its deeper skin penetration may be desirable [33]. On the other hand, octyl methoxycinnamate must remain on the skin surface as it is a sunscreen [59].

Furthermore, liposomes improve formulation stability as well as reduce oxidation of oxidation-susceptible cosmetic ingredients. Cysteamine-loaded liposomes had lower oxidation. As cysteamine has a whitening effect, it may be employed in hyperpigmentation disorders [29]. Similarly, vitamin C and folic acid co-loaded in chitosan-coated liposomes had lower sunlight degradation. Besides, the additional chitosan coating provided an even greater antioxidant ability [26].

As the nanoformulations are designed for skin application, clinical studies are highly recommended to prove their efficacy. In that regard, vesicular carriers improved melasma [28, 32] and skin hydration [56]. Aspasomes [32] and a semisolid bearing resveratrol and n-butylresorcinol encapsulated liposomes [28] reduced melasma in a clinical assessment [28]. Regarding hydration, a cream containing goat milk in liposomes decreased transepidermal water loss. In addition, because there were changes in pH skin, this nanotechnology-based product might be important to prevent barrier function disruption [56].

Cationic carrier is mostly reported as the most suitable one for improving skin penetration [26, 60, 61]. Despite that, anionic liposomes were the most suitable ones for acid ascorbic than cationic liposomes. Anionic ascorbic acid liposomes provided a greater collagen synthesis as well as increased cell uptake, which suggests that the use of anionic carriers for hydrophilic molecules may be a better approach [30].

Therefore, it is essential to conduct a proper physicochemical evaluation prior to nanoformulations development, in order to improve its performance [30].

Recently, the association of polymers and vesicular formulations has been proposed as a strategy to increase carrier stability [31]. In this sense, hydroxyethyl cellulose enriched transfersomes, hyaluronan enriched transfersomes and a hybrid system combining liposomes and poly(3-hydroxybutyrate) had greater physicochemical stability over storage [31, 35]. Accordingly, hybrid systems development may be an interesting approach to obtaining nanocosmetics with higher shelf life [35].

5. Conclusion

Several nanotechnology-based cosmetics have been developed in order to achieve more effective products, with an emphasis on vesicular carriers. Beyond the benefits provided by nanocarriers, nanocosmetics have attracted cosmetic industry interest as they have high market value that may reflect an increased purchase by market consumption.

Therefore, skin delivery of cosmetic ingredients via nanocarriers provides a better alternative to traditional cosmetics by improving skin hydration, skin penetration and stability in addition to their higher versatility. Moreover, herbal-based nanocosmetics may improve patient compliance and have higher biocompatibility, as well as biodegradation potential. Additionally, natural-based nanocosmetics are more environmentally friendly.

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