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Review

Clay minerals: Properties and applications to dermocosmetic products and perspectives of natural raw materials for therapeutic purposes—A review

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ABSTRACT

Clay minerals are layered materials with a number of peculiar properties, which find many relevant applications in various industries. Since they are easily found everywhere, they are particularly attractive due to their economic viability. In the cosmetic industry, clay minerals are often used as excipients to stabilize emulsions or suspensions and to modify the rheological behavior of these systems. They also play an important role as adsorbents or absorbents, not only in cosmetics but also in other industries, such as pharmaceuticals. This reviewer believes that since this manuscript is presented as covering topical applications that include pharmaceuticals, some types of clay minerals should be considered as a potential material to be used as drug delivery systems. We review several applications of clay minerals to dermocosmetic products, relating them to the underlying properties of these materials and exemplifying with a number of clay minerals available in the market. We also discuss the use of clay minerals in topically-applied products for therapeutic purposes, specially for skin treatment and protection.

1. Introduction

Natural raw materials intended for topical application have always been subject of research and development studies, aiming for a variety of uses in the cosmetic and pharmaceutical industries, as evidenced by the large number of skin care products launched constantly in the market. Also Clay minerals have been object of many studies in a large variety of areas, such as geology, cosmetology, materials science, pharmaceutical sciences, medicine, food science and biotechnology.

Among the more than four thousand known minerals, around thirty are currently used in the pharmaceutical and cosmetic industries (Carretero and Pozo, 2010). In particular, clay minerals have been increasingly utilized in dermocosmetics and major advances have been achieved in the research and innovation related to these materials. Environmental awareness has reflected in an increased interest in the use of clay minerals, because they cause no harm to the environment after disposal and can be easily found everywhere (Viseras et al., 2007a).

The unique properties of clay minerals have attracted great interest of the industry, specially because these materials are both abundant and economically viable (Auerbach et al., 2004). Despite the importance of clay minerals in the development of novel dermocosmetic products, detailed review papers concern to the use of clay are still scarce in the scientific literature. This paper serves the purpose of filling this gap at an introductory level.

Clay minerals are natural crystalline earthy materials of fine grain size (less than 2 μm of particle size) composed chemically of hydrated aluminum silicates, with magnesium, iron, calcium, potassium or sodium present as essential constituents, organized in different fashions as superimposed alternating layers. In addition to clay minerals, clays may also contain organic compounds, soluble salts, quartz particles, pyrite, calcite, other non-clay minerals and amorphous components (Auerbach

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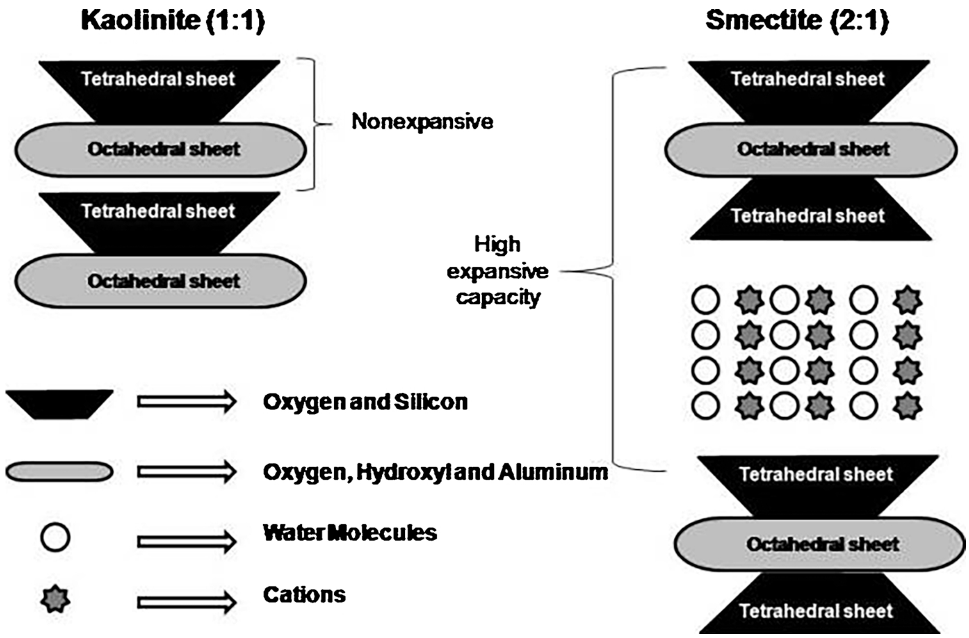

Fig. 1. Models of a 1:1 (Kaolinite) and 2:1 (Smectite) sheet structures, respectively.
Adapted from Leroy and Revil (2004).

et al., 2004).

The medicinal and dermocosmetic uses of clay date back to prehistory. Ocher clay mixed with water and different types of mud were once used by early humans for wound healing and skin cleansing. In Mesopotamia and ancient Egypt, the so-called medicinal earths (nowadays identified as clay) were used as therapeutic agents for wound treatment and suppression of bleeding. Cleopatra of Egypt is known to have applied slime from the Dead Sea on her facial skin for aesthetic purposes. Nubian earth was used by Egyptians as anti-inflammatory and mud materials were utilized for mummification of corpses (Gomes and Silva, 2007).

Clays are easily found in nature and all over the world. They occur in different colors (Stepkowska and Jefferis, 1992) such as white, red, beige, yellow, brown, *etc*. and may be used for many purposes (Murray, 2007), among which are those related to personal care or health care, when they are directly applied on the skin or mucosae or when added to dermocosmetic or pharmaceutical products for topical application. Each clay mineral has a unique cosmetic or therapeutic function, such as wound healing, skin lightening, embellishment, sebum absorption, antisepsis, moisturization, vascularization and toxin elimination (Gomes and Silva, 2007). Before they can be utilized in the manufacturing process of dermocosmetics, clay minerals extracted from natural sources need to be processed in order to attain maximum purity and ideal grain size (desiccation, pulverization, sieving and wet separation of the clay fraction, sterilization by heat, *etc*.) (Murray, 2007). In some cases, the clay minerals may be subjected to a chemical process to enhance some specific property (as it is the case with the so-called homoionic clay minerals) or even change their behavior (such as with the organo clay minerals) (Paiva et al., 2008).

Nowadays, one can identify the presence of clay minerals in a large variety of dermocosmetic products, such as facial creams, sunscreen, products for skin cleansing, shampoos and makeup items (liquid and powder foundations, eye shadow, facial masks, lipsticks, *etc*.). The ever-increasing use of clay minerals in dermocosmetic products either as dermatological active ingredients or as excipients is due to the versatility of these materials and to the peculiarity of their physical and chemical properties (López-Galindo et al., 2007).

In accordance with the purpose of their use, clay minerals must fulfill standards for their chemical, physical and toxicological specifications, such as: purity, particle size, texture, stability, chemical inertia, water content, atoxicity, safety and microbiological purity. Different applications of clay minerals in pharmaceuticals or dermocosmetics include their roles as *"abrasives, absorbents, adsorbents, anticaking agents, glidants, coating agents, opacifying agents, viscosity-increasing agents, emulsion stabilizers, binders, suspending agents, therapeutic agents, tablets and capsule diluents or lubricants"* (Carretero and Pozo, 2010).

The aim of this review is to provide the reader with essential information about the state-of-the-art of the applications of clay minerals in the skin care field. These work reviews the structural organization and the main features of clay materials, the different applications of a number of clay minerals available in the market to dermocosmetics and the use of clay minerals in topically-applied products for therapeutic purposes.

2. The structure and the main properties of clay minerals for dermocosmetic applications

The mostly important properties attributed to clays for dermocosmetic applications are 1) the surface properties: surface area, cation exchange capacity or CEC, layer charge (either neutral or charged), sorption, dispersability; 2) rheological properties: thixotrophy, rheopecty, viscosity, plasticity; and 3) other physical and mechanical properties: particle size, shape, color, softness, opacity, reflectance, iridescence and so on.

Clay minerals are phyllosilicates containing two types of sheets, structurally organized in units named tetrahedral sheet (T) and octahedral sheet (O). The cations present in each sheet and the substitutions in them may lead to a net charge deficit that can depend on the type of sheet (T or O) and on the type of substituting cations (the substitutions are basically driven by the ion size, charge and other atomic properties). The type of substitution affects the behavior of the clay in regard to adsorption capacity and rheological properties (Auerbach et al., 2004; López-Galindo et al., 2007).

Clay minerals of the 1:1 and 2:1 types (Fig. 1) acquire totally different conformations when they are dispersed in polar solvents such as water. Clay minerals of the 1:1 as well as most 2:1 clays like talc, pyrophyllite, illite, palygorskite and sepiolite type do not swell when in contact with a polar solvent while chlorites very occasionally swell, smectites and vermiculite do. The smectites swell easily, forming a gel structure with well-defined rheological properties and displaying a pseudoplastic behavior (Viseras et al., 2007a).

The utility of a clay mineral in specific applications are due to their physical and chemical properties, which are mainly dependent on two factors: (a) their crystal structure, which can be either a 1:1 structure (one tetrahedral sheet bound to another octahedral sheet) or a 2:1 structure (one octahedral sheet between two tetrahedral sheet) and (b) their chemical composition (Carretero and Pozo, 2010; Viseras et al., 2007a; Auerbach et al., 2004; Murray, 2007; Christidis, 2011). Additional factors are important in determining the properties and applications of a clay. These are the non-clay mineral composition, organic material content, the type and amount of exchangeable ions and soluble salts, and the texture (Murray, 2007).

Kaolinite is one of the most common clay minerals sources. Its structure is of the 1:1 type and consists of alternating sheets of tetrahedral silica and octahedral alumina. This structure is highly organized and well balanced, with little or no ionic substitution and thus low cation exchange capacity. The ion-exchange capacity of kaolinite varies within the range of 3–15 mEq/100 g (Auerbach et al., 2004). Although the minerals of the *kaolin* group display a relatively small specific surface area in comparison to those of other clay groups, they can still adsorb small molecules, proteins, bacteria and viruses on the surface of their particles (Schiffenbauer and Stotzky, 1982). Except for halloysite (tubular) the other kaolin minerals occur in pseudohexagonal plates. They are white or nearly white in color. Other significant qualities of this group are their opacity, softness and non-abrasiveness. Due to its shape and size (nanotubes) as well as its surface properties atoxicity and high mechanical strength and modulus, halloysite nanotubes (HNTs) have a great potential; they are currently investigated and have various commercial applications as additives in polymers and plastic, electronic components, controlled drug delivery vehicles, dermocosmetics and in home and personal care products (Kamble et al., 2012; Saif and Asif, 2015; Pasbakhsh et al., 2013).

Rheology studies show that kaolinite exhibits a peculiar rheological behavior in comparison to other clay minerals. Rheology tests with kaolinite at 70% dispersed in water have shown that this material acquires a dilatant behavior when subjected to shear stress, *i.e.*, the apparent viscosity increases according to the shear rate. The origin of this behavior is the proximity of the dispersed particles and their interactions while the shear stress is being applied (Viseras et al., 2007b). The rheological behavior is affected by the crystal morphology and the surface charge (Bergaya et al., 2006).

Talc is one of the most important in the pharmaceutical and dermocosmetic markets, because both its high sorption and fluidity make it particularly useful to a large diversity of applications. Talc is composed of hydrated magnesium silicate in a 2:1 structure – more specifically, an octahedral sheet of magnesium between two tetrahedral sheets of silica. It is odorless and can be easily micronized to become a white powder of ideal particle size. Owing to its ability to absorb oils and fats, talc is widely used in facial makeup to control the skin oiliness (Piniazkiewicz et al., 1994; Yekeler et al., 2004).

Clay minerals of the *Smectite* group are interesting to be used in the pharmaceutical and cosmetic industries due to their peculiar properties, such as their greasy aspect, odorlessness and color that varies among yellow, pink and grey (Carretero and Pozo, 2010; López-Galindo et al., 2007).

The *Smectite* group is composed of several types of clay minerals that differ in origin and chemical composition. The latter directly relates to the technological properties and to the cosmetic applications of these materials. The structure of this type of clay is 2:1, consisting of a central octahedral sheet of alumina lying between two tetrahedral sheet of silica. The structure allows multiple substitutions in each sheet. Most of the technological uses of smectite are referred to their high cation exchange capacity (CEC), a reactions that take place in the interlayer space by exchangeable cations such as Na^+, K^+, Ca^{2+} and Mg^{2+} which balance the negative 2:1 layer charge (Murray, 2007; López-Galindo et al., 2007). These groups of minerals also have a very large surface area.

Smectite clays are commonly hydrated due to polar molecules such as water which are permitted into the gap between layers (the interlayer), so that the volume of the structure expands (swells) substantially with respect to the dry bulk. As a result, the material exhibits a rheological behavior known as thixotropic, which is desirable for some dermocosmetic applications (López-Galindo et al., 2007). Montmorillonite, one of the *smectite* minerals, is the most abundant clay used to organoclays synthesis due to properties such as swelling behavior, adsorption and large surface area and high cation exchange capacity. This type of clay can exhibits high penetration of water or dermocosmetic active ingredients between the layers. This ensures chemical stability, controlled release and dermocosmetic or pharmaceutical efficiency of any active ingredients carried by the clay (Paiva et al., 2008). Also Smectite gels are sensitive to the addition of strong electrolytes once its particles are negatively charged and the process of flocculation occurs in the presence of electrolytes or when positively charged suspensions are included (Viseras et al., 2007a).

Bentonite is the industrial name of rocks composed almost only of smectites. There are two types of commercial bentonites for industrial use, namely calcium bentonite and sodium bentonite. Both swell in water as do all smectites, but the latter does it considerably much more (Viseras et al., 2007b).

Rheological tests conducted during hydration of smectite show that the viscosity increases significantly and very rapidly within a certain time interval, after which the viscosity continues to increase at a slow rate. This decrease in the growth rate of the viscosity is due to the fact that the remaining free particles take more time to find an available site in the structure after the hydration. When the hydrated clay is subjected to pressure or shear stress, a large portion of its structure is broken down (Viseras et al., 2007b).

Clay minerals of the *Fibrous* group have a structure of the 2:1 ribbon-like structure, where the tetrahedral sheet periodically inverts, making the octahedral sheet discontinuous and thus resulting in parallel channels along the particles. Due to the channels, these minerals have a high internal surface area, high sorptive capacity and high viscosity (Murray, 2007). The amount of water in these materials varies from 5 to 27% in palygorskites and from 17 to 34% in sepiolites. The fibers can be easily dispersed in water or other polar solvents. This dispersion produces a bulky suspension that displays high viscosity (López-Galindo et al., 2007). The viscous dispersion formed from these fibrous clays can retain its stability even in the presence of highly concentrated electrolytes (López-Galindo and Viseras, 2004). In the pharmaceutical and cosmetic industries, this kind of behavior is particularly desirable in the manufacturing of emulsions, which must comply with stability standards.

Sepiolite (known in the market as magnesium trisilicate) and palygorskite known in the market by the name of attapaulgite active clay occur as crystals in the shape of flexible elongated needles, which can easily disperse in water or other polar solvents so as to form a three-dimensional lattice throughout the entire liquid (Carretero, 2002). Most of the production of palygorskite occurs in the countries of the Western world, where one million tons are produced every year. The crystal structure of this clay is more rigid than that of sepiolite, affecting its rheological behavior and its applicability in the industry (Viseras et al., 2007a).

The clay minerals described above illustrate how diverse these materials are in terms of their properties. This richness is a consequence of all the different possibilities of arranging chemical elements in two different types of layered structures (2:1 or 1:1) and is reflected in the large number of applications of clay minerals in various industries. In the next section, several important industrial applications will be described.

3. Modification of clay minerals and their application to other industries

Clay minerals contain elements that are essential for life and, in particular, for human beings, also these materials can be obtained easily and are found everywhere in the world. According to (Velde, 1995): *"clay minerals, the most abundant and chemically active components of the surface mineral world, are the key to understanding the links between nature (life), its substrate (essentially silicates), and a mastery of the total ecosystem by man."* (p. v of the preface).

As already mentioned, clay minerals are particularly versatile materials due to their high ion-exchange capacity, large surface area, swell capacity, ability to delaminate, non abrasiveness, softness and small size of their particles, which are naturally charged and therefore interact via relatively strong electrostatic forces (Zhou and Keeling, 2013). When they are dispersed in water, the medium becomes viscous and can exhibit a number of possible rheological responses, such as plasticity, pseudoplasticity, thixotropy, dilatancy, *etc*. These materials occur naturally in many different colors and can be applied on the skin or mucosae for aesthetic or dermocosmetic treatment (Lukham and Rossi, 1999).

The high cation-exchange capacity of clay minerals allows them to be organophilized to enhance their properties for pharmaceutical and dermocosmetic applications. By this method, clay minerals can be engineered into new materials, opening up the possibility of new applications. Clay minerals that have been subjected to the organophilization process are named organoclays and are synthesized by means of cation exchanges within the layered structure. For instance, a cation can be replaced by a cationic surfactant such as quaternary alkylammonium salt (Fig. 2), which is the most used surfactant in the preparation of organoclays. The applications of organoclays are in accordance with their properties; they can function as *"adsorbents, rheological control agents, paints, grease, cosmetics, personal care products, oil well drilling fluids, etc.* (Paiva et al., 2008).

The insertion of foreign molecules into the layers of a clay mineral is limited by its cation-exchange capacity. Clay minerals are hydrophilic but this deceases with the increasing size of the exchangeable cations both in the series of the alkaline and of the alkaline earth cations. Hydrophobicity is reached by exchange with organic cations such as alkylammonium (Christidis, 2011). Not only does the insertion of molecules change the chemical structure of a clay mineral, but it also increases the basal spacing between the layers. This affects the properties of the material, particularly the adsorption capacity (Paiva et al., 2008; Coelho et al., 2007; Kakegawa and Ogawa, 2002).

In order to be selected for organophilization, the clay minerals must have some specific properties, such as a high cation-exchange capacity, swell capacity when in contact with polar solvents, certain adsorption properties and a large surface area. Smectites are particularly useful for organophilization, specially montmorillonite and also hectorite which is already being organophilized by some companies for commercial purposes. Other types of clay minerals are also being investigated for use in organophilization, such as sepiolites and synthetic mica (Paiva et al., 2008).

Clay minerals can also be used for improving the environmental quality, since they can function as catalysts in natural chemical reactions. Also clay is used in an enormous variety of industrial processes in a diversity of industries such as paint industry, ceramic industry and oil industry, where specially the montmorillonite clay mineral find applications as drilling fluid due to their swell capacity and their hygroscopic property (Zhou and Keeling, 2013; Jackson, 1998; Sparks, 2005).

The past years have seen an increasing interest in utilizing clay minerals as carriers for drugs that can be adsorbed and released at a later time in target locations of the human body, thus permitting the controlled delivery of active ingredients. This idea has also been considered for applications to gene therapy and vaccines. Additionally, the interaction of drugs with biomolecules and clay minerals can be useful for determining the impact of residual pesticides and medications on the environment (Zhou and Keeling, 2013).

Halloysites have gained prominence in the field of nanotechnology applied to the pharmaceutical industry, by virtue of their tubular morphology that can potentiate the effect of dermocosmetic or pharmaceutical active ingredients. The structure of such clay minerals makes them ideal drug carriers, as they occur as nanotubes that can accommodate molecules in their interior. This allows for the controlled delivery of substances in target locations of the human body. The physical and chemical properties of halloysites (such as the level of impurities and the volume of the internal cavity of the nanotubes) vary greatly among samples obtained from different sources, to the extent that some of them may be suitable for use as a carrier but others may not (see the study conducted by Pasbakhsh et al., 2013).

4. The different properties of clay minerals in relation to the development of topically-applied products

From ancient times, human beings have used clay minerals, albeit somewhat empirically, for such purposes as healing and protecting the skin against solar radiation. Today, a great deal of scientific information about clay minerals is available and the pharmaceutical and cosmetic industries have an increasing interest in incorporating this natural resource to their products. The use of clay minerals for such applications as pelotherapy, mudtherapy and fangotherapy has also become increasingly popular over the past years (Viseras et al., 2005; Cerezo

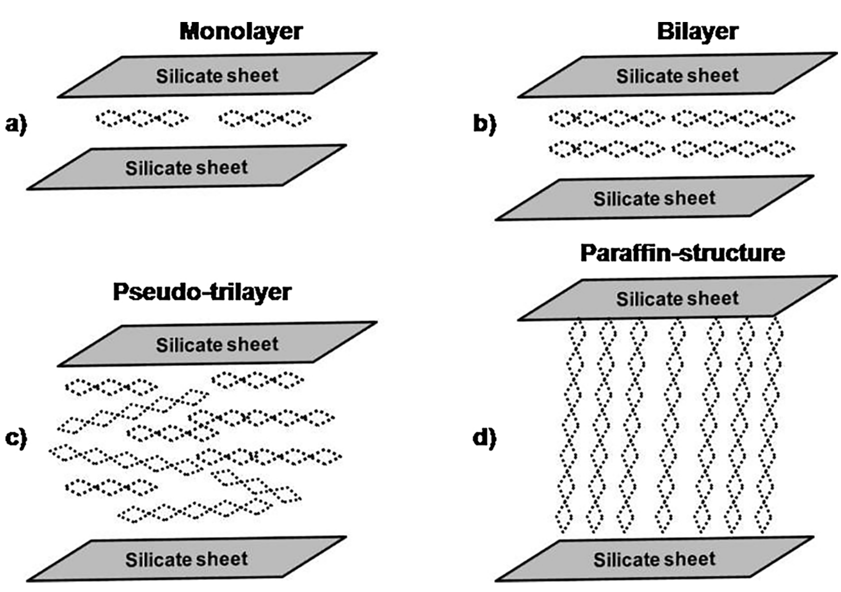

Fig. 2. Orientations of alkylammonium ions in the galleries of silicate sheets: (a) monolayer, (b) bilayers, (c) pseudotrimolecular layers, and (d) paraffin-structure arrangements of alkylammonium ions.
Adapted from Bergaya et al. (2006).

et al., 2005; Ghadiri et al., 2015). Owing to their absorption and adsorption capacities, clay minerals can be used as effective poultices in the treatment of swelling, edema and inflammation (Velho et al., 1998).

The American and European pharmacopeias include guidelines for the use of a number of clay minerals in pharmaceutical and dermocosmetic formulations, namely kaolinite, talc, smectite, montmorillonite, saponite, sepiolite and palygorskite. The existence of monographic records of these specific clay minerals in pharmacopeias is not only due to their extensive use in the industry, but also for their compliance with certain standards that are required for human use (López-Galindo et al., 2006).

The pharmaceutical and cosmetic industries use clay minerals either as excipients or as agents in their products. Clay minerals are present in many different kinds of formulations, such as tablets, capsules and powders (oral administration), ointments, creams, fluid emulsions and suspensions (topical administration). In the cosmetic industry, the main application of clay minerals is as an excipient to adjust the rheological properties and to stabilize emulsions by avoiding coalescence of oil and water droplets. Clay minerals act as a barrier in between these droplets, ensuring the physical-chemical stability of the system (Viseras et al., 2007a).

Smectite or montmorillonite (namely known as bentonite) has been used as a suspending and emulsion agent for a long time and it is the most widely used in the cosmetic industry for stabilization of emulsions. Besides acting as a barrier that prevents coalescence, it can also modify the rheological behavior of the emulsion, resulting in a final product with features that are both acceptable and desirable to consumers (Viseras et al., 2007a; Teixeira-Neto and Teixeira-Neto, 2009; Soleymani et al., 2016).

Palygorskite, sepiolite, kaolinite, smectite and talc produce an opaque effect and have a high sorption capacity, which are the reasons why they are widely used in such dermocosmetic formulations as creams, powders and emulsions. These clay minerals ensure the opacity of the formulations, help remove skin oiliness together with toxins and also help cover up skin maculae and patches (Viseras et al., 2007b; Teixeira-Neto and Teixeira-Neto, 2009).

Clay minerals of the mica group such as Illite of high reflectance and iridescence, which makes it the most widely used in the manufacture of makeup products such as eye shadows and lipsticks. Recently, micas of the muscovite type have been used in the production of moisturizing creams in order to create a skin brightening effect (Carretero and Pozo, 2010).

Because of their peculiar physical and physical-chemical properties, clay minerals are widely used in the pharmaceutical and cosmetic industries as a raw material in product development. Examples of different roles played by these materials in industrial applications are presented in Table 1. Clay minerals with a high index of refraction are used in the development of sunscreens that can block UVA and UVB radiations. Those that are highly dispersed in water are used as an ingredient in such products as toothpaste and bath salts. Those that are hard enough are used as abrasives in toothpastes. Clay minerals can also be used as astringents, which are major components of deodorants. As mentioned previously, properties like high sorption, large specific surface area, opacity and high reflectance favor the utilization of certain clay minerals in formulations like emulsions and powders (Carretero and Pozo, 2010; Yekeler et al., 2004).

5. The use of clay minerals in topically applied products for various treatments

Even before the industry started to incorporate clay minerals in cosmetic products, these materials were already used in geotherapy and fangotherapy at aesthetic clinics and spas. Several skin conditions and inflammations such as ulcers, comedos, acne and seborrheic dermatitis can be treated efficiently with clay masks, thanks to the ability of some clay minerals to adsorb dirtiness, oiliness and toxins. Warm clay applied on the skin causes an increase of both perspiration and sebaceous secretion, thus favoring pore dilation and consequently promoting the excretion of toxins (Carretero and Pozo, 2009; Clijsen et al., 2008).

Three clay-based products with curative properties, intended for topical application in balneotherapy, dermopharmacy and dermocosmetics, have been under development by Gomes and Silva, 2007. One of them contains a blend of bentonite of the Porto Santo Island (in the Madeira archipelago) with biogenic carbonate sand of Porto Santo. The bentonite plays the role of an excipient, promoting the adhesion of the active component (in this case, the sand) to the skin. The biogenic carbonate sand contains such elements as Ca, Mg and Sr, which are released into the skin in a controlled manner until they reach the extracellular matrix, where cellular metabolic and catabolic chemicals also circulate.

Another product has been developed by Gomes and Silva, 2007 which contains bentonite gel and several chemical elements present in the biogenic carbonate sand of Porto Santo, intended for topical use in the treatment of certain rheumatic diseases. The same authors also mention a third product that they were developing based on a blend of many ingredients, among which biogenic silica (the active component), refined bentonite from Porto Santo and sodium hydroxide (pH conditioner). According to them, the silicon provided by the biogenic silica is essential for the synthesis of collagen fibers and therefore helps treat osteo-articular and muscular-skeletal affections.

One experimental study conducted by Cohen et al., 1976 showed the effect of samples of sterile montmorillonite clay implanted into

Table 1
Clay minerals most commonly used in topically-applied products (modified from Carretero and Pozo, 2010; López-Galindo et al., 2006).

Clay Mineral/Formula/Layer Type	Pharmaceutical Nomenclature	Chemical Nomenclature	Application
Kaolin/$Si_2\ Al_2O_5(OH)_4$/1:1	Kaolin	Hydrated Aluminum Silicate	dermocosmetic creams, facial masks, powders, emulsions and makeup products
Talc/$Mg_3Si_4O_{10}(OH)_2$/2:1	Talc	Talc	makeup products, formulations for hair removal, deodorants, soap and baby powders
Smectite Group/$(Al_{1,67}Mg_{0,33})Si_4O_{10}(OH)_2M^+_{0,33}$/2:1	Bentonite/Purified Bentonite	Aluminum Magnesium Silicate	emulsions, makeup powders and sunscreen
Ilite/$KAl_2(Si_3Al)O_{10}(OH)_2$/2:1	Mica	Potassium Aluminum Silicate	eye shadow, makeup products and lipsticks
Palygorskite/$(Mg,Al,Fe^{3+})_5(Si,Al)_8O_{20}(OH)_2(OH_2)_4{\cdot}4H_2O$/2:1	Attapulgite	Aluminum Magnesium Silicate/Magnesium Aluminum Silicate	facial masks, emulsions, powders and dermocosmetic creams
Sepiolite/$Mg_8Si_{12}O_{30}(OH)_4(OH_2)_4{\cdot}8H_2O$/2:1	Magnesium Trisilicate	Hydrated Magnesium Trisilicate/Magnesium Aluminum Silicate/Anhydrous Magnesium Trisilicate, Magnesium Metasilicate, Magnesium Ortosilicate	facial masks, emulsions, makeup powders and dermocosmetic creams

incisions made on the backs of laboratory rats. It was found that the clay samples induced a significant increase in the relative rate of collagen synthesis (5.4 ± 0.6) as compared to the rate of the control group (2.9 ± 0.4) and to the rate of the group that received sterile sand in their incisions instead of clay (3.1 ± 0.3).

Another study, conducted by Valenti et al., 2011 showed that the topical application of kaolinite clay masks in rats promoted an increase in the amount of collagen fibers in their skins. The group of rats that received skin treatment with clay masks for a period of 7 days displayed a significant increase in the percent area of collagen fibers (51.74 ± 1.28%) in comparison to the control group (43.39 ± 1.79%). A third group of rats, which received skin treatment with retinoic acid for the same period of time, displayed a statistically insignificant increase in the area of collagen fiber (45.66 ± 1.10%) in comparison to the control group. The authors conclude that clay could be useful for skin rejuvenation, as corroborated by their findings.

Solar radiation, particularly UVA and UVB, and its impact on unprotected skin has been subject of much scientific discussion and has increasingly aroused interest in substances that can provide protection to the skin. The detrimental effects of UVA and UVB on the skin can be as serious as the development of malignant carcinomas in the cutaneous tissue, so it is fair to say that sunscreen is a dermocosmetic product of great importance to the skin health. Thanks to their excellent properties, some clay minerals have been included in dermocosmetic formulations of sunscreens, acting as a barrier that blocks the solar radiation and thus protects the cellular DNAs against potentially serious damage that could cause many diseases. In order to be useful for sunscreening, the clay minerals must have high index of refraction and optimal light dispersion properties. The bentonite clay and the hectorite organoclay have been shown to meet the required specifications and are already being used as sunscreen (Ghadiri et al., 2015; Mattioli et al., 2015).

6. Conclusion

Clay minerals have a wide variety of applications in many industries and are particularly important in the development of pharmaceutical and dermocosmetic formulations, for a number of reasons. The different roles played by these materials in formulations include, but are not limited to, topical administration of active molecules, controlled release of drugs, cosmetic treatment and more recently, protection against UVA and UVB solar radiation. Moreover, the peculiar properties of clay minerals make them useful excipients that can help stabilize emulsions and suspensions, as well as modify the rheological behavior of emulsions. Their high sorption and ion-exchange capacities allow them to be organophilized in order to enhance or even change certain properties that are needed for specific applications.

Even though the research on clay mineral has been able to attract great interest of the pharmaceutical and cosmetic industries and to make room for greater use of this type of material in various applications, little information is available on the effects of clay minerals on the human body, particularly when they are applied on the skin. Therefore, more studies that focus on the development of new clay-based dermocosmetic formulations together with detailed analyses of their physical-chemical stability are needed. More specifically, these studies should include, for instance, permeability testing, *in vitro* and *in vivo* cytotoxicity assays and analyses of the interaction with solar radiation. Such experimental work will be essential to assess the efficiency and therapeutic safety of novel clay-based products, thus allowing them to be eventually introduced in the market.

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