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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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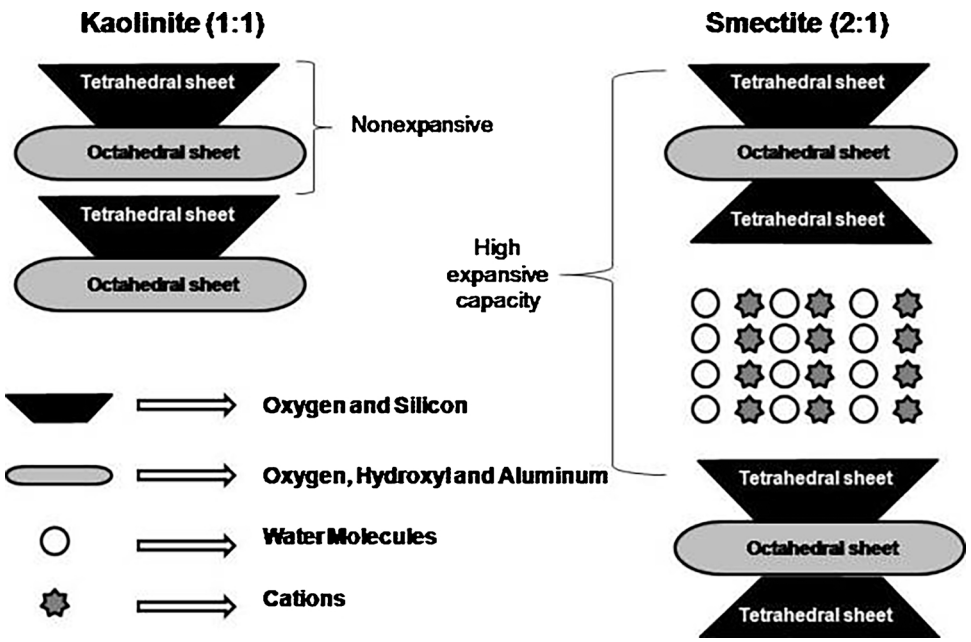

Fig. 1. Models of a 1:1 (Kaolinite) and 2:1 (Smectite) sheet structures, respectively.
Adapted from Leroy and Revil (2004).

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