Review article

Harnessing organoclays: Advancements and perspectives in cosmetics and personal care products

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ABSTRACT

The use of clay minerals for curative, decorative or protective purposes is old as mankind. Advancements in the design and production of modified clays have enhanced their applications. "Organoclays" are nanocomposite materials formed by the association of clays with cationic surfactants through an intercalation process. Consequently, organoclays are dispersible in non-aqueous environments, therefore expanding their versatility. This review focuses on the cosmetic and personal care field, where organoclays can act as functional ingredients on formulations and packaging. Organoclays can be found in make-up and skincare products, with a particular presence in sunscreens. Although the current scientific literature on cosmetic packaging and organoclays is scarce, their usefulness in food packaging could be extended to cosmetics and personal care products. This extension may bring innovative properties such as tailored polymer degradation rates and improved color pay-off. The chemical association of different clay minerals allows the creation of cutting-edge ingredients with synergistic properties. Their usefulness as polymer functional ingredients is already being exploited to produce sustainable, ecofriendly packaging. Along the same line, future research efforts could also revolve around eco-friendly, non-contaminant biosurfactants for new organoclays' synthesis.

1. Introduction

Clay minerals have been integral to traditional healthcare practices for centuries, revered for their diverse therapeutic properties across cultures worldwide. In fact, clays have been, and remain, ingredients in pharmaceutical and cosmetic formulations, acting both as active ingredients and excipients (e.g., gastrointestinal protectants, skin actives, cleansing ingredients, sun protection, or as excipients carrying other actives such as medicinal waters, etc. (López-Galindo et al., 2011; Gomes et al., 2021; Viseras et al., 2021). Clays have a well-deserved place in health and beauty routines since prehistoric humans began to use colours as camouflage with hunting, hiding, instilling fear, for spiritual or social purposes. Homo erectus and Homo neanderthalensis used ochres mixed with water and different types of mud to cure wounds, soothe irritations and cleanse the skin. Some of these uses were "learned" by mimicking the behavior of some animals that instinctively

used them for similar purposes (Carretero, 2002; Viseras et al., 2021). Focusing on improving physical appearance, the ancient Egyptians used ointments, including clays, to cleanse and soften the skin (i.e. Queen Cleopatra used Dead Sea mud for beauty purposes; ancient Romans used kaolin powder to make their skin paler). Clays have also played a crucial role in geotherapy(Carretero, 2002; Gomes et al., 2013), acting as excipients of thermal water treatments, that continue to be used to this day.

In current cosmetics and personal care products, clay minerals are used as actives in face masks due to their high adsorption capacity, enabling them to eliminate grease and toxins (Moraes et al., 2017). They are also present in creams, powders, and emulsions, acting as antiperspirants, opacifiers (both to the formulation and to the skin), shine removers, and blemishes coverers (Viseras et al., 2021).

Nowadays, clays intended for pharmaceutical or cosmetic uses must comply with certain quality standards determined by purity, safety, and

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reproducibility. Additionally, some clays are subjected to chemical processes to increase or modify their physicochemical properties and behavior, as is the case with organoclays (OC)(Viseras et al., 2007).

2. Organoclays

Organoclays (OC) are hybrid nanomaterials formed by the association of natural clay minerals with organic surfactants and/or other organic compounds through an intercalation process (de Paiva et al., 2008; Park et al., 2011; He et al., 2014; He and Zhu, 2017; Phuekphong et al., 2020). According to The Clay Minerals Society (CMS) an "*organoclay is a phyllosilicate, typically smectite, vermiculite, or kaolin, but also other minerals (e.g., double metal hydroxides) with sorbed organic molecules, such that the properties of the mineral are altered. Commonly, the sorption occurs between the 2:1 or 1:1 layers*" (The Clay Minerals Society Glossary for Clay Science Project, 2018).

The differential feature of OC versus natural clays is their higher hydrophobicity and specific surface area. Natural clay minerals are hydrophilic in nature, capable of retaining high amounts of water and "swell" (when the clay has a laminar structure). On the contrary, OC are hydrophobic and thus able to disperse and interact more effectively with organic compounds and solvents. The hydrophilic/hydrophobic balance of the final OC depends on the length and packing density of the alkyl chains. The resultant OC features are mainly affected by the properties of the pristine mineral, which in turn, depend on its origin (mineral deposit, weathering conditions, paleographic and sedimentation settings) (He et al., 2014; Perelomov et al., 2021). Some authors highlighted that the OC's absorption efficiency is determined by defects in the crystal lattice, the interlayer cation composition, and their CEC.

One of the most important factors to consider is that bivalent cations lead to stronger interactions between clay layers. For instance, calcium-rich montmorillonites suffer from lower structure expansion (smaller interlayer spaces) than sodium ones. Likewise, smectites with divalent cations suffer from slower exchange ratios than monovalent ones (Perelomov et al., 2021). Therefore, clay minerals with higher CEC can retain greater amounts of organic molecules, making them better candidates for organomodification (i.e. montmorillonite vs. kaolinite or palygorskite) (Sarkar et al., 2019).

Moreover, the properties of the intercalated organic substance (MW, length, and functional groups) are also determinant for OC performance (Perelomov et al., 2021).

2.1. Synthesis of organoclays

The synthesis of OC is based on the effective reaction between the mineral and the organic compounds (Goyal and Jerold, 2023). Depending on the nature of the organic molecules, several interaction mechanisms can be involved, such as ion-dipole interaction, hydrogen bonds, acid-base reactions, electrostatic interaction, van der Waals forces, zwitterionic, among others (Paiva et al., 2008; Intasaard et al., 2018; Guo et al., 2020; Goyal and Jerold, 2023; Massaro et al., 2024).

Generally, the OC's synthesis can be classified into dried-state synthesis and aqueous synthesis (Lagaly, 1994; Kozak and Domka, 2004; Guégan, 2019a). For the former one, solid-solid interactions are forced, and the OC are combined with the organic molecules by different strategies without using any solvent. For instance, the solid-state reaction between the dry clay and the cationic modifier inside a ball mill(Guo et al., 2020). During the milling process, interactions between the organic molecule and clay particles are forced, something that can be controlled by modifying either the proportions of compounds or the milling conditions. This type of OC synthesis can lead to more heterogeneous results (not all the clay enters in proper contact with the organic compound), though they are more convenient for industrialization (Ogawa et al., 1990; Breakwell et al., 1995; Khaorapapong et al., 2002; Beall and Goss, 2004; Yoshimoto et al., 2005; Bergaya et al., 2006; Guo et al., 2020; Garikoé and Guel, 2022). As an alternative, semi-solid-state

reactions have also been reported, but comparison studies did not reveal any significant improvement with respect to the dry organomodification (Guo et al., 2020).

The aqueous solution OC synthesis (or cationic exchange) is the easiest and most effective method. A standard procedure would include the dissolution of the cationic surfactant in the appropriate dissolution medium. In parallel, the clay is dispersed in water (Phua et al., 2013). After clay aqueous dispersion, water molecules surround the clays' exchangeable cations, leading to clay swelling. This increases clay surface and facilitates the interaction with surfactants (Guégan, 2019a). Then, the clay suspension is slowly added to the organic compound solution. The clay and organic compound ration is usually determined by the clay Cationic Exchange Capacity. With this method, the introduction of organic cations to the interlayer occurs quickly, even at room temperature, just needing the assistance of stirring or sonication (Phua et al., 2013; Guo et al., 2020). Nevertheless, the use of high temperatures can improve the resultant organomodification, reason why some authors have reported the use of microwave heating with ultrasonic dispersion (Guo et al., 2020) or simple magnetic stirring at 80 °C (Phua et al., 2013). The obtained precipitate is usually collected/separated by filtration or centrifugation. Further purification steps such as excess of salts removal can be done by stirring in plain water, something that can be repeated several times on a case-by-case basis (Phua et al., 2013). This procedure is also employed for fibrous clays organomodification, even if these clays are unable to expand or "swell" under water (Verge et al., 2013).

Other methods such as binding of inorganic and organic anions, grafting of organic compounds (Yılmaz et al., 2021), acidic reactions, pillaring by poly(hydroxo-metal) cations, intraparticle and interparticle polymerization, delamination and reaggregation of smectites, and physical treatments (lyophilization, ultrasound and plasma) (Bergaya et al., 2001) can also be used. The purification method or the organomodified clay can vary depending on the procedure and on the organic compound used. As an example, reactive grafting could include the refluxing in chloroform and filtration in cold methanol (Phua et al., 2013). As an additional example, Jiang and co-workers grafted sepiolite (fibrous clay mineral) with 9, 10-dihydro-9-oxy-10-phosphaphenanthrene-10-oxide (DOPO) (Jiang et al., 2019). Firstly, sepiolite was mixed with and 3-aminopropyl triethoxysilane in toluene at 90 °C, separated by filtration and washed with different organic compounds. Afterwards, the DOPO grafting was performed in toluene medium and at the same temperature, followed by a similar purification procedure.

2.2. Classification of organoclays

The most basic classification of organoclays is based on the structure of the mineral, its expansion and surface charge capacity, as suggested by the Perolomov's review (Perelomov et al., 2021). Based in those characteristics the organoclays can be classified as 1:1 phyllosilicate and 2:1 phyllosilicates (Fig. 1A). For the 1:1 group (represented by kaolinite) the organomodification is limited due to their inability to expand (clay minerals without interlayer space). In this group only clays of the kaolinite subgroup interact with organic molecules, while the serpentine ones being "inactive" for this purpose. For kaolinite organomodification the soft chemical method is commonly used. It consists of grafting short alkyl chains to kaolinite by melting and aggregation. Halloysite also belongs to the kaolinite subgroup, but in this case, the hydrogen bonds stacking the 1:1 layers are weaker, making halloysite interlayer organomodification possible (Perelomov et al., 2021).

Phyllosilicates with 2:1 structure are the most common OC, especially smectites such as montmorillonite (MMT), saponite, and hectorite. MMT has held the limelight in the preparation of OC because of its moderate charge density and CEC, swelling ability, and propensity for organic compounds intercalation (He et al., 2014; Perelomov et al., 2021).

Unlike other 2:1 clay minerals, like sepiolite and palygorskite, which
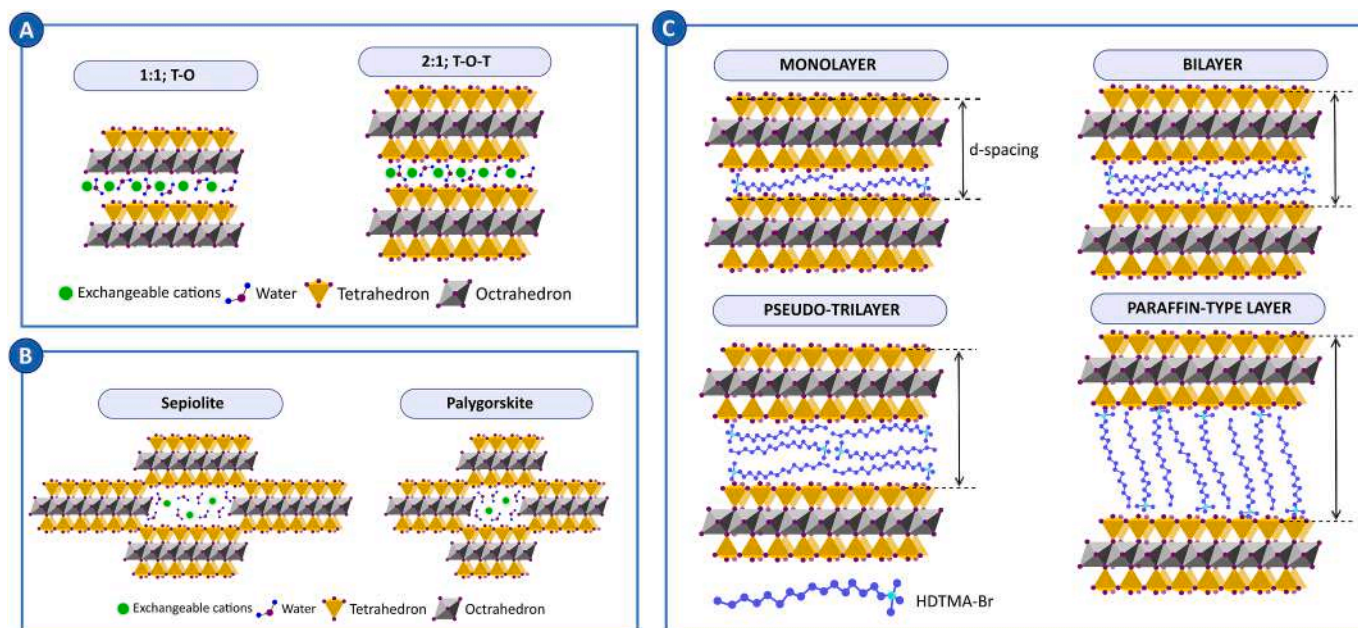
Fig. 1. Natural clay minerals structure include tetrahedral sheets (in yellow) and octahedral sheets (in grey). A) Phyllosilicates 1:1 or (T-O) and phyllosilicates 2:1 (T-O-T). B) Structure of T-O-T fibrous clays sepiolite and palygorskite. Modified from (Garcia-Villen et al., 2021). C) Possible arrangements of long chain quaternary ammonium cations (HDTMA-Br) in the interlayer space of a smectite. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

lack interlayer spaces, their crystalline structure and high surface area make them promising for various applications. They feature a continuous tetrahedral sheet where every 6 units (sepiolite) or 4 units (palygorskite, also known as "attapulgite") the tetrahedron suffer a 180° inversion, causing a discontinuous octahedral sheet (Fig. 1B). These discontinuities create zeolitic channels parallel to the fibre length, where protons, water and exchangeable cations are located(Garcia-Villen et al., 2021). Due to their inability to expand, organomodification is restricted to their external surface (Phuekphong et al., 2020). Nonetheless, there are some studies that pointed out the possibility of cationic surfactants penetration into the zeolitic channels of sepiolite (Karataş et al., 2013). Surface modification of palygorskite and sepiolite usually entails surface modification with organic cations (such as ammonium salts, alkylamines or stearic acids) or by grafting with other species such as organosilane (Ruiz-Hitzky et al., 2011; Jiang et al., 2019; Meng et al., 2024). The surface organomodification of these clays is favoured by the high amount of silanol groups available (higher than smectites). The organosilane grafting of sepiolite and palygorksite favour the dispersibility of these clays in low-polarity compounds, usually present in cosmetic and personal care products (Meng et al., 2024).

The organomodification of synthetic layered silicates and polysilicates, such as magadiite, kenyaite(Lagaly et al., 1975; Maejima et al., 2007; Jones and Coughlin, 2008), ilerite (Ishii and Shinohara, 2005), kanemite(Takahashi and Kuroda, 2011), among others, can also be mentioned. These inorganic ingredients behave similarly to smectite clays. Although some sources/patents mention them as part of cosmetic and some personal care products (Iwasaki et al., 2000), the amount of literature references combining their organomodification and cosmetic use is still scarce. Nevertheless, due to their synthetic and so, pure nature, they could be a promising option as new functional ingredients of cosmetic and personal care products. A comparative study between montmorillonite and palygorskite organomodification (with octadecyl trimethyl ammonium chloride (C18) and dimethyl dioctadecyl ammonium chloride, DC18) revealed different structural arrangements (Fig. 2A). For these organomodified clays, the oil-dispersion of palygorskite was easier than montmorillonite (Fig. 2B), showing higher stability; on the contrary, organomodified montmorillonite performed better rheological profiles, especially for DC18 organomodification (Fig. 2C) (Zhuang et al., 2017).

According to the surfactant used, OC are classified into Cationic Organoclays, Zwitterionic Organoclays, and Nonionic Organoclays (Guégan, 2019a). Similarly, the Clay Mineral Society distinguishes between two groups: adsorbent OC, also known as adsorptive-type OC, and the organophilic OC (The Clay Minerals Society Glossary for Clay Science Project, 2018).

Adsorbent organoclays are smectites where the natural inorganic counterions have been replaced by short-chain organic cations such as tetramethylammonium, tetraethylammonium, and trimethylphenylammonium as well as alkylamines (Lagaly et al., 1975; Takahashi and Kuroda, 2011). These cations effectively maintain the clay interlayer in an open state, enhancing the adsorption capacity of larger organic compounds. This approach has been investigated for the adsorption of organic contaminants(Guégan, 2019b; Phuekphong et al., 2020; Perelomov et al., 2021) as well as carriers of different therapeutic actives.

Organophilic OC includes all clay minerals with large exchanged organic-cation alkyl groups. Specifically, they are obtained from the intercalation of long-chain quaternary ammonium ions with the general chemical formula $[(CH_3)_3\,NR]^+$or $[(CH_3)_2NR]^+$, where R represents the alkyl hydrocarbon(de Paiva et al., 2008; He et al., 2014; Perelomov et al., 2021). The substitution of the primary interlayer cations alters the original clay properties. OC possess both hydrophilic and hydrophobic surfaces along with a large porosity and surface area (Guégan, 2019b; Perelomov et al., 2021).

As a conclusion, the current market for commercially available organoclays includes a variety of modified clays, primarily based on montmorillonite. Organoclays are widely used in industries like coatings, drilling fluids, rheology adjustment, thermal stability, and barrier properties. Additionally, OC are playing an important part in water remediation, due to their ability to interact with non-polar contaminants (Phuekphong et al., 2020).

2.3. Structure of organoclays

In 1969, Lagaly and Weiss deduced that the intercalation and
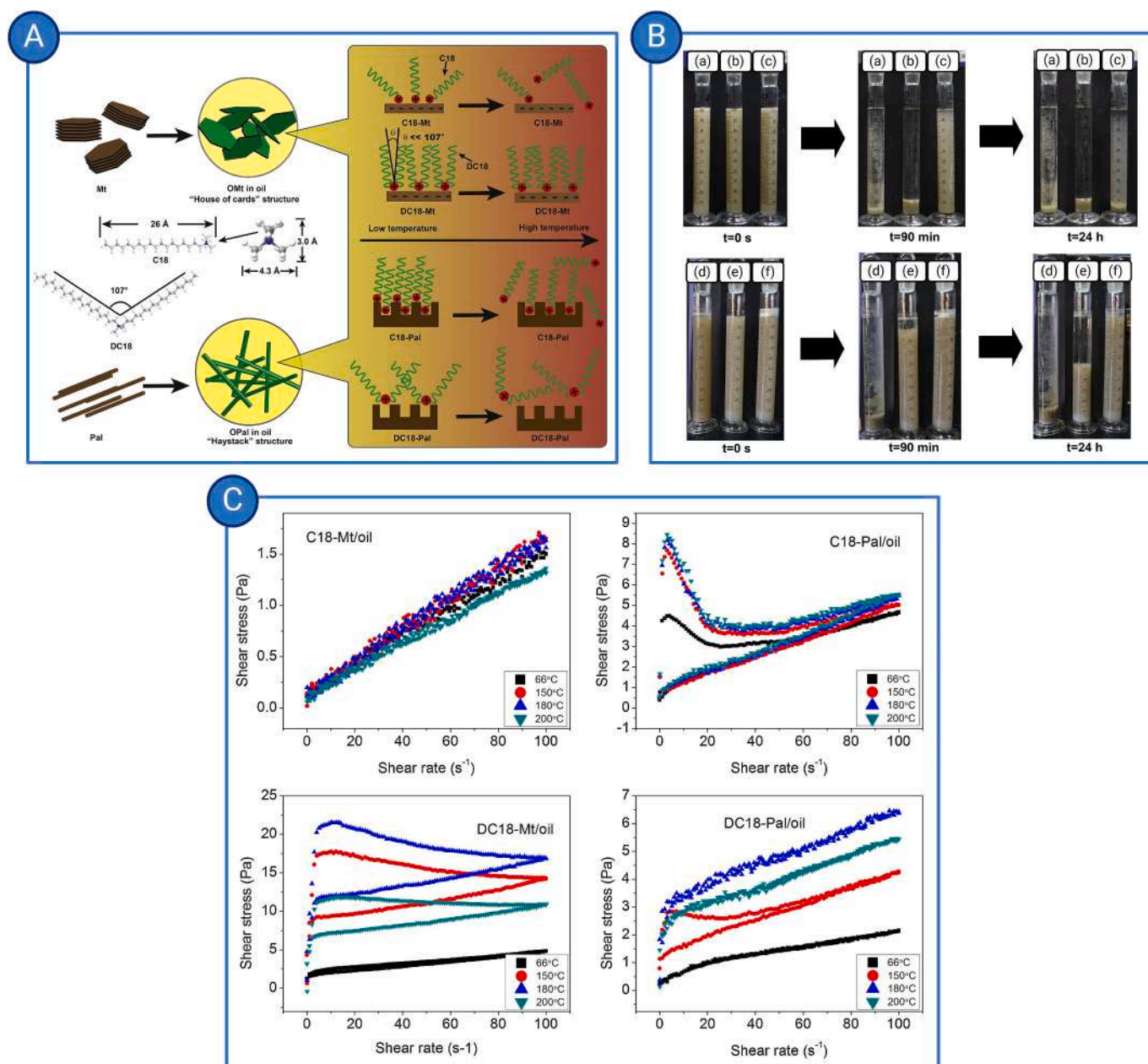
Fig. 2. A) Schematic representation of the structural changes and structural arrangement of organomodified montmorillonite (OMt) and palygorskite (OPal). C18 and DC18 were compared for both clays, inducing different surface properties. B) Macroscopic comparison of OMt and OPal dispersibility in oil at different time-points. (a) Mt., (b) C18—Mt, (c) DC18-Mt, (d) Pal, (e) C18-Pal and (f) DC18-Pal. C) Flow curves of C18 and DC18 organomodified montmorillonite (left curves) and palygorskite (right curves). Extracted from (Zhuang et al., 2017).

orientation of organic chains in OC are determined by i) the charge of the clay interlayer, ii) organic molecule length, iii) surface geometry of clay, iv) the exchange angle (Lagaly and Weiss, 1969).

Organic chained substances or flat molecules arrange into one or more layers parallel to the mineral surface, thereby expanding the interlayer space of the original smectite (Lagaly et al., 2013; Guégan, 2019a). For example, the distance between these layers, which is typically less than 1.3 nm with clay with Na⁺ saturated clay, increases to more than 2.2 nm after organomodification. During this process, "intercalated" or "exfoliated" nanocomposites are produced(Bardziński, 2014). Organic ions can lie flat on the clay surface, forming monolayer, bilayer, pseudo-trilayer or adopting a paraffin-like structure (Paiva et al., 2008). Fig. 1C schematically illustrates potential arrangements of long-chain quaternary ammonium cations in smectites.

A stable monolayer structure is achieved when the concentration of quaternary ammonium cations is close to the CEC, while two-layered (Fig. 1C) and three-layered chains may appear with higher organic concentrations. The transition from monolayer to double layer is influenced by the chain length and the uniformity of silicate charge distribution (Lagaly et al., 2013; Perelomov et al., 2021). In the presence of long-chain alkylammonium and quaternary ammonium ions or alkyl-amine groups, a pseudo-three-layer arrangement (Fig. 1C) can form. Here, the positive charge of the surfactant binds to the silicate layer, while the alkyl portion acquires curved trimolecular rearrangement. High-charge smectites and vermiculite allow the formation of a paraffin-like arrangement (Fig. 1C), generating higher interlayer space (obtention of OC/polymer nanocomposites), see Fig. 3A (Sarkar et al., 2019; Perelomov et al., 2021).
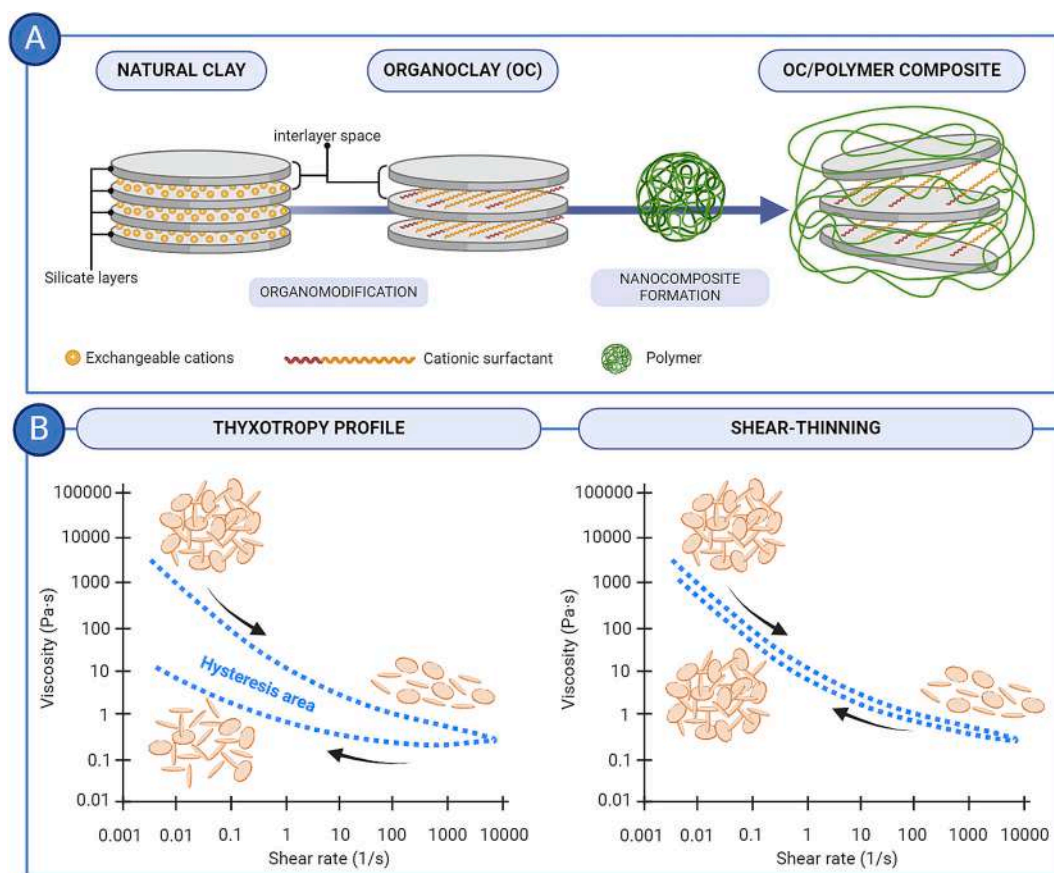
Fig. 3. A) Changes in clay structure during organomodification and polymeric composite formation. B) Differences in clay minerals internal network structure depending on their thixotropic or shear-thinning profiles when subjected to shear rates (schematic viscosity vs. shear rate flow curves). Created with BioRender.

3. Organoclays in cosmetics and personal care products

The worldwide cosmetic market is forecasted to be worth 131 billion U.S dollars by 2026 (Petruzzi, 2014) and is expected to expand at a compound annual growth rate of 4.2 % from 2023 to 2030 (GVR, 2022). Currently, the Asian Pacific cosmetic market accounts for the largest market share (nearly 44 % in 2022) (GVR, 2022). In Europe, the cosmetics and personal care products market reached €88 billion in retail sales price in 2022 (Cosmetics Europe: Personal Care Association). This sector is estimated to have a high socio-economic impact, contributing at least €29 billion annually to the European economy and supporting over 3.6 million jobs. Factors driving this growth include evolving fashion trends, substantial product innovation, advancements in packaging (GVR, 2022). The rapid expansion of the market has underscored the need to develop more efficient and environmentally sustainable products(Huang, 2019; Salvioni et al., 2021; Goyal and Jerold, 2023).

Some reports predict that "the adverse consequences of routine use of cosmetic goods due to the inclusion of dangerous chemicals are anticipated to limit market expansion" (GVR, 2022). This has prompted major brands to invest in research and innovation (R&I) to secure their leading market position in the long-term. According to Colipa "cosmetic companies spend 5% of their sales on research". Goyal and co-workers recently published a review highlighting the importance of bio-cosmetics, noting that many conventional formulations use non-biodegradable ingredients, such as petroleum-based ones (Goyal and Jerold, 2023). Consequently, one of the primary current efforts in the cosmetic industry is focused on developing green cosmetics (in formulation and packaging) where ingredients, such as clay minerals, can play a crucial role.

3.1. Functionalities of natural clay minerals in cosmetics

It is imperative to comprehend the inherent properties and activities of natural clays, as these attributes can be transposed to OC, thereby enhancing or modifying their characteristics. These properties include small particle size, varied chemical composition, high exchange capacity (CEC) through different types of exchangeable cations (and anions), large surface area, and ability to interact with different molecules, making them suitable for carrying and releasing different actives. Additionally, clays are naturally abundant, non-contaminant, biocompatible, have low toxicity (in vitro and in vivo), and possess opacity and astringency, all of which make them suitable for skin contact (Choy et al., 2007; Viseras et al., 2007; López-Galindo et al., 2011; Becker et al., 2013; da Rocha et al., 2022).

The extensive roles of natural clay minerals in cosmetic have already been reviewed by various authors (Choy et al., 2007; López-Galindo et al., 2007, 2011; Carretero and Pozo, 2010; Aguzzi et al., 2013; Cerezo et al., 2013; Sánchez-Espejo et al., 2014; Iannuccelli et al., 2016; Daneluz et al., 2020; García-Villén et al., 2020c; Viseras et al., 2021; Wargala et al., 2021). Clays are widely used in sun care products, toothpastes, creams, powdery formulations, emulsions, face masks, deodorants, hair cosmetics, and nail polishes (Carretero and Pozo, 2010). Moreover, there is an extensive scientific literature proving the usefulness of these clays as stabilizers for chemical substances (drugs, cosmetic actives), emulsions and suspensions (da Rocha et al., 2022). Layered Double Hydroxides (LDH) have reported to stabilize retinoic acid, ascorbic acid, and tocopherol, and to be effective carriers for different vitamins and organic UV absorbents for human skin (Perioli et al., 2006; Choy et al., 2007). LDH have been shown to enhance PABA stability and effectiveness, preventing its absorption into the skin, thus increasing sunblock safety (Perioli et al., 2006).

High amounts of silicon in clay contribute to tissue hydration and anti-inflammatory properties for the skin. Aluminum, also present in high amounts in clay minerals, has been reported to have healing activity, hydration benefits, and melanin adsorption capabilities. Other beneficial properties of clays, such as bactericidal, antiseptic, and regenerative effects, are linked to elements like Cu or Zn present in natural clay minerals (Martsouka et al., 2021). Additionally, natural clays can treat conditions such as acne, ulcers, and other inflammatory skin disorders (Wargala et al., 2021), helping to mattify the complexion and regulating excess oil production due to their high surface area.

Studies on the benefits of natural origin products traditionally used as cosmetics, like Dead Sea Minerals, have revealed that clays like kaolinite had cleansing, antiaging, remineralizing properties, and blood circulation stimulation(Portugal-Cohen et al., 2015).

Talc is reported as one of the most used clay minerals in cosmetic due to its absorbent, anticaking, filler, and opacifying properties. According to Wargala et al. talc is present in up to 30 % of deodorant products, 35 % of aerosol make-up bases, 99 % of baby powders and 100 % of face powders (Wargala et al., 2021).

Decorative cosmetics have also utilized clay minerals, especially mica. This mineral provides a metallic appearance, color, and shine, making it a common ingredient in eyeliners, mascaras, lip products and eye shadows (Ohta, 2006).

3.2. Functionalities of organoclays in cosmetics

OC have improved cosmetics performance, especially in sensory attributes, product stability and the shelf-life of biocomposites and nanocomposites (Grigale-Sorocina and Birks, 2019; Goyal and Jerold, 2023). The transition from hydrophilic to hydrophobic properties in OC improves their interactions and chemical compatibility with most cosmetics formulations, which usually include multiple phases (oil-based and water-based) (GVR, 2022; Han et al., 2011).

The use of OC in cosmetic field is relatively recent, dating back to the 1970s. Their roles are closely tied to their rheological properties, such as thixotropic or shear-thinning profiles, viscosity and yield stress enhancement (Grigale-Sorocina and Birks, 2019). Terms like "rheology ingredient", "suspending agent", "thickener", "viscosity controlling" are frequently used interchangeably by many authors, which can confuse non-expert readers. This confusion is understandable since a "suspending agent" plays a specific role different from a "thickener", but all these functions stem from the OC's rheology profiles. The inclusion of organoclays, like hectorite and bentonite, in decorative cosmetics has reported better color retention and color-coverage in nail lacquers, lipsticks, and eye shadows, improving quality and customer satisfaction (Patel et al., 2006; Grigale-Sorocina and Birks, 2019).

The liquid dispersion of clay minerals and OC, at the right concentration, produces non-Newtonian, pseudoplastic, yield stress fluid with thixotropic or shear-thinning profiles. Thixotropy is a time-dependent shear-thinning property ascribed to those fluids showing higher viscosities under static conditions but that become thinner (less viscous) under shear-stress (agitation, application, pumping). When the stress is removed, shear-thinning fluids immediately regain their original viscosity, whereas "thixotropic" fluids take some time to do so. Consequently, thixotropic flow curves exhibit a hysteresis area, unlike shear-thinning samples (Fig. 3B). This area is generated due to the time-dependency, indicating that the internal fluid structure requires time to restructure after the removal of stress.

One of the first patent including OC was owned by Colgate Palmolive Co. (US4113852A) who developed an antiperspirant deodorant requiring a precise thixotropic rheology profile (Bar-Shalom, 1988). The formulation utilizes OC to achieve an innovative pseudoplastic, shear-thinning formulation consisting of a weak, oily OC-gel formed in static conditions. This OC-gel easily "break" on shaking before usage to facilitate product application. After application, the OC-gel's internal network resembles, ensuring that the antiperspirant remains homogeneously dispersed (Bar-Shalom, 1988; Barel et al., 2009). Additional research by Cao and Butcher, highlights that Bentone® hectorite clay exhibits remarkable thixotropy properties, making it particularly suitable for cosmetics, including sunscreens (Cao and Butcher, 2006). This property can also be translated to other smectite OC as well.

Yield stress is defined as the minimum stress required for a material to start flowing (Møller et al., 2006). Smectite dispersions are characterized as yield stress fluids, a property that is closely related to their shear-thinning and thixotropic properties (Møller et al., 2006; Jimenez et al., 2021). The usefulness of these properties is undeniable for topical application, since these thixotropic, yield stress products are easily spreadable and they stay put on the application site for longer when the stress is removed. It is important to stress out that these properties are obtained at a certain concentration and level of clay particle dispersion, also depending on the type of clay and dispersant used.

"Pre-dispersed gel cosmetics", also known as "master gels" or "pre-made gellants/thickeners" consist of a pre-activated OC dispersion (10-40 %) with a carrier oil formed by silicone fluid, organic oil and a polar activator (or polar solvent). These master gels simplify the formulation process of creams, lotions, mascaras, liquid make-up, antiperspirant aerosols, requiring only low to medium shear mixing (Qcheng Lin, 2005). The quaternary groups of these formulations enhance the dispersibility of the OC in solvents of different polarity. However, to achive effective dispersion and viscosity, the OCs must first be activated with a polar activator such as propylene carbonate or ethanol (Laba, 1993). The concentration of the polar activator is crucial, since an excess may disrupt the gel network structure (Barel et al., 2009; Chiarentin et al., 2023). Several commercial master gels combine OC with propylene carbonate as a polar activator in various cosmetic oils: BENTONE GEL® VS-5 V (cyclopentasiloxane, disteardimonium hectorite and ethanol), BENTONE GEL® TN V (C12-15 alkyl benzoate, stearalkonium hectorite and propylene carbonate), and BENTONE GEL® LIP V (hydrogenated polyisobutene, disteardimonium hectorite and propylene carbonate).

These commercial OC-based ingredients are suitable for both anhydrous cosmetics and water-in-oil emulsions. In the former case, they enhance viscosity, impart thixotropy and shear-thinning and stabilize suspensions (e.g. of insoluble pigments). Consequently, they can be found in anhydrous cosmetics such as lipsticks, pencils, and nail polishes. When added to emulsions, they are also known as "self-emulsifying gels" and take part of the oil phase (increase viscosity and prevent syneresis), usually combined with other emulsifiers or waxes. Under these circumstances, the emulsifiers form the micelles within the OC-gel matrix, which prevents micelles coalescence, thus being less prone to phase separation (Fig. 4A).

The organomodified bentonite (Tixogel MP250) and two montmorillonites (MMT) modified with octadecylammonium and octylammonium ions were combined with reactive epoxy/amine mixtures (Le Pluart et al., 2004). The interactions between the dispersant monomer and the clay vary, leading to different rheological properties. High or intimate interactions between OC and monomer result in high viscosity fluids while poor interactions correspond to low viscosities.

In 2011, Hato and co-workers studied how the type of surfactant affects OC rheology (Hato et al., 2011). They examined three OCs (Cloisite 15 A, Cloisite 25 A and Cloisite 30B) with different degrees of hydrophobicity dispersed in silicone oil, a common cosmetic ingredient. All suspensions exibited non-Newtonian, shear-thinning behavior and more viscous than silicone oil alone. Cloisite 15 A, with the highest hydrophobicity, showed the most significant viscoelastic characteristics due to stronger OC-silicone interactions. Cloisite 25 A exibited "intermediate" behavior between Cloisite 15 A and Cloisite 30B (Hato et al., 2011).

In addition to their rheological functions, OCs can fulfil other roles in cosmetics. For example, Cloisite-Na and its organomodified counterpats (Cloisite 20 A and Cloisite 30B) were tested for antibacterial activity after being grafted with antibacterial salts such as dimethyl
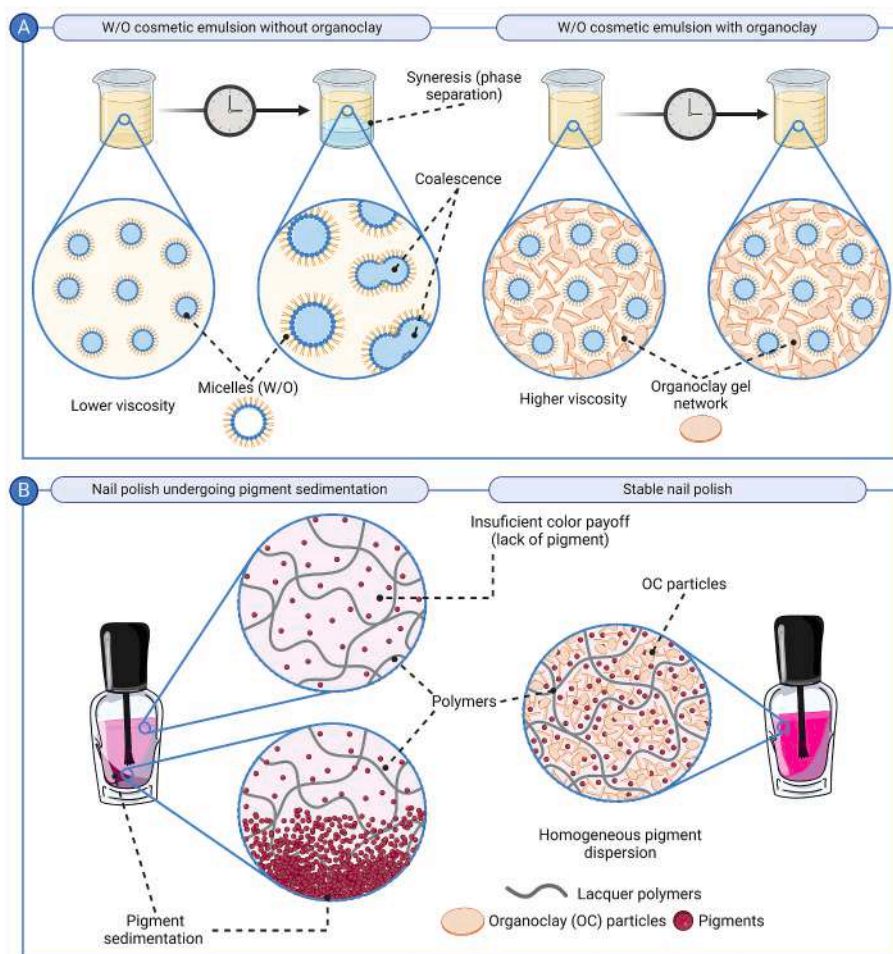
Fig. 4. A) Schematic representation of OC as thickeners and emulsion stabilizers. The coalescence of W/O micelles is prevented by the gel-like internal network formed by OC dispersed in a hydrophobic ambience. B) Schematic representation of OC roles as pigment dispersant. Left) Nail polish formulation undergoing pigment sedimentation due to lack of adequate rheology properties. Right) Stable nail polish formulation where pigment particles remain homogeneously dispersed thanks to the internal network structure created by OC. Figure created with BioRender.

dehydrogenated tallow, quaternary ammonium and methyl tallow, bis-2-hydroxyethyl, quaternary ammonium (Hong and Rhim, 2008). These modified OCs were evaluated against *Staphylococcus aureus*, *Listeria monocytogenes* (Gram +), *Salmonella typhimurium*, and *Escherichia coli* (Gram -) using the Agar diffusion test. The antimicrobial activity of the MMT OC is ascribed to the release and diffusion of cationic surfactants. Cloisite 30B and Cloisite 20 A demonstrated both bactericidal and bacteriostatic activities, unlike Cloisite-Na, which did not show such properties (Hong and Rhim, 2008). Other, less commonly used clays such as magadiite has been used for their antibacterial activity. In fact, the combination of magadiite and ammonium ions gave rise to a microbicidal ingredient patented in 2007 by Maejima and co-workers (Maejima et al., 2007).

Chlorhexidine is frequently added to cosmetic and other personal care formulations as antimicrobial(Opstrup et al., 2015). The combination of chlorhexidine acetate with MMT creates an organomodified MMT with intrinsic, broad-spectrum antimicrobial activity (He et al., 2006). This approach is beneficial for developing anti-acne cosmetics or personal care products, serving as rheological modified with preservative properties, allowing the reduction or elimination of additional preservatives. Moreover, the controlled release of chlorhexidinefrom this OCs results in 31 % release over 72 h (Meng et al., 2009). Holešová et al., developed chlorhexidine diacetate organomodified claysthrough a two-step process. First, they modified smactites by remplacing their interlayer cation with Zn^{2+}, Cu^{2+} and Ag^{2+}. Then, they dispersed these

modified clays in a clorexidine solution to achive organomodification. These OCs showed effective antimicrobial activity against *E. coli*. Additionally, Ag and Zn-organomodified vermiculites were particulary effective against *E. faecalis* compared to their unmodified counterparts. Against resistant *P. aeruginosa*, Ag-organomodified MMT and Cu-organomodified vermiculite showed better results (Holešová et al., 2013).

Nunes Pessanha and co-workers (Savas and Hancer, 2015) studied an alternative method to obtain antibacterial OCs. They organomodified MMT with cetyltrimethylammonium bromide (CTMA) and Ag, and then mixed it with low density polyethylene using a screw extruder process. The resulting film exhibited better inhibition properties against *E. coli* than the silver clays alone. This enhanced antibacterial effect is attributed to the electrostatic forces between negatively charged bacteria and the positively charged OC surface due to the presence of Ag (Savas and Hancer, 2015). This result could be of great usefulness not only for cosmetic formulations but also for cosmetic packaging with intrinsic antimicrobial properties.

3.3. Organoclay in skin care

The treatment of many skin diseases can benefit from the complementary use of cosmetics. From conditions such as dermatitis, psoriasis or rosacea, combining drug therapy with appropriate cosmetics, such as moisturizing creams, non-aggressive detergents, can significantly

improve outcomes. A 2001 study demonstrated this by using quaternium-18-bentonite in a moisturizing, emollient cream for occupational chronic hand dermatitis (Fowler, 2001). The study found that 28/33 individuals significantly improved their condition and were able to reduce or eliminate the use of topical steroids.

Additionally, Spadini and co-workers. Patented a cleansing implement for skin or hair that contains various formulations. These include moisturizing cleansing formulations, wash-off moisturizer, lotion, water-activated hair bleaching and water-activated depilatory formulation, all incorporating 15 % of Bentone™ 38 ISD GEL OC(Spadini et al., 2003). This illustrates the versatile use of OCs in both therapeutics and cosmetic applications.

The organopolysiloxane copolymer patented by Limura and Furukawa was considered a raw material for cosmetic formulations providing higher stability, good water resistance, sebum resistance, glossiness, tactile sensation and/or adhesive properties to the hair and/or skin. Different MMT OCs are mentioned as part of the formulation (Iimura and Furukawa, 2010). Contemporary patents also highlight the use of OCs as flow enhancers in powdered solid cosmetics at concentrations ranging from 1 to 15 % *w*/w (Kaneko et al., 2010) and as emulsion adjuvants in water-in-oil-type cosmetics (Sasaki and Omura, 2010).

Additionally, Sharma and Argawal incorporated OCs into anti-dandruff formulations, where they act as rheology modifiers and suspending agents for zinc pyrithione (Sharma and Agarwal, 2014). Zinc pyrithione is an active ingredient with antimicrobial activity against *Malassezia yeast (a common cause of* dandruff) has limited solubility and is often formulated as a suspension. The inclusion of OCs guarantees the homogeneous dispersion of zinc pyrithione in these formulations.

Organomodified palygorskite was tested for healing properties (Da Silva M.L. et al., 2014). Two ammonium salts were tested (dimethyl benzyl ammonium chloride alkyl and cetyl trimethyl ammonium chloride) and proved better interactions with skin during wound healing, which results promising for dermopharmaceutical purposes, including cosmetics.

3.4. Organoclays in sunscreens

According to the European Regulation, a sunscreen is defined as "any preparation (creams, oils, gels, sprays) intended to be placed in contact with the human skin (…) to protect it from UV radiation by absorbing, scattering, or reflecting radiation" (EU, 2009). Sunscreen products play a specific protective role in protecting human health due to the clear correlation between UV exposure and skin cancer (Perugini et al., 2019), with approximately 50 to 70 % of melanomas being related to UV radiation. Broad-spectrum UV photoprotection is essential to prevent short and long-term solar radiation damage (Dzwierzynski, 2021).

Sunscreens are classified based on their mechanisms into physical (mineral) and chemical (organic) filters. Physical filters, such as clay minerals (kaolin) and other inorganic ingredients (TiO_2 or ZnO) act by reflecting or blocking UV radiation. In contrast, chemical filters transform UV energy into heat, which can lead to the production of ROS (photocatalytic activity), subsequently damaging DNA. Their absorption is notably affected by the sunscreen formulation and should be prevented (Gubitosa et al., 2020; Dzwierzynski, 2021).

There are also strong indicators relating skin ageing with excessive or uncontrolled sun exposure (Guan et al., 2021), meaning that sunscreen actives can also be found in other cosmetics and personal care products to prevent skin photoaging(Dudley et al., 2021). These products, known as "secondary sunscreens", often incorporate sunscreen agents to provide additional protection(Gubitosa et al., 2020). Natural clay minerals and OCs are widely used in sunscreen formulations due to their effectiveness as sun protection agents. Their advantages include stability against UV radiation, non-allergenic properties, and low photocatalytic activity, making them suitable for both primary and secondary sunscreen applications (Biondi et al., 2007). Natural clays obtained from

different regions of Kenya were formulated as hydrophobic pastes and evaluated as sunscreen (Ng'etich et al., 2014). Authors disclaimed that their protection ability (reporting sun protection factor (SPF) values from 1.46 to 40.98) was influenced by Fe_2O_3, TiO_2 and ZnO concentrations, although no exact mineralogical composition is provided (Ng'etich et al., 2014). More recently, unmodified anionic clays (LDH) have been evaluated as SPF boosters of Tinosorb®S Lite Aqua, Uvinul® T 150 and Uvinul® A Plus. In this case, the LDH boosting effect was correlated with particle diameter, which determines the optical UV scattering (Chen et al., 2024).

Good, aesthetic properties and other consumer-friendly attributes of sunscreens, such as easy application and the absence of whitening effect, improve compliance (Dudley et al., 2021). Rheology is a key factor influencing consumer acceptance and compliance with sunscreens. An easy-to-apply, flowable formulation ensures a pleasant experience and enables a more uniform and homogeneous distribution, enhancing effectiveness. Yamaguchi and co-workers. Studied the viscosity of a sunscreen to improve its application and performance (Yamaguchi et al., 2021). They evaluated petrolatum, dextrin palmitate, silica silylate, and quaternium-18 hectorite OC as thickeners for the sunscreen oil-phase. Quaternium-18 hectorite provided the most effective and uniform application over a skin-mimicking substrate, preventing the production from flowing into the creases and wrinkles, thus improving viscosity and resulting in higher UV absorbance (Yamaguchi et al., 2021).

"SPF boosters" are ingredients that enhance the radiation filtering effect of the active substance increasing SPF and allowing for a reduced concentration of UV filters. Biological sources for SPF boosters currently under study include extremophiles like *Bacillus lysate* and plants such as green coffee oil and lignin (Lorquin et al., 2021; Landry et al., 2023). A good SPF booster should possess minimal or negligible UV radiation absorption, be safe for the environment and human health, and compatible with the sunscreen formulation. Inorganic filters like TiO_2, ZnO, silica and alumina can enhance the UV absorption efficiency of organic UV filters. Nevertheless, some inorganic filters, such as TiO_2, have reported photocatalytic activity, which can degrade the accompanying organic filters (Chen et al., 2024). Clays and OCs can act as SPF boosters for both physical and chemical UV filters without exhibiting photocatalytic activity. Egambaram and co-workers. Demonstrated that natural clay minerals could counteract the photocatalytic activity and the formation of oxygen reactive species associated with ZnO and TiO_2, making them valuable additives in sunscreen formulations to enhace stability and effectiveness (Egambaram et al., 2019).

Regarding the SPF-boosting effects of OCs, bentonite and hectorite (both natural and organomodified) produced by the Elementis Company were evaluated as ingredients in various sunscreens formulations (Cao and Butcher, 2006). The results showed that all tested formulations containing OCs reported higher in vitro SPF values compared to formulations without OCs. Additionally, the hydrophobic nature of OCs improved the water resistance of the sunscreens, which is a valuable attribute for enhancing sunscreen performance. Thixogel® MP 100 OC was successfully included in a patented, sprayable formulation (carnauba wax emulsion) to prevent fruit sunburn. The addition of emulsified OCs significantly increased the formulation's reflectivity, a property that can be transferred to skin sunscreens formulations (Schrader, 2011).

The importance of guaranteeing sunscreen's physicochemical stability is beyond dispute, especially since these products are often exposed to extreme environmental conditions (i.e. high temperatures). Different Bentone® Gels successfully prevented the separation of an oil-in-water sun care formulation for one month under stressful conditions (40 °C) (Cao and Butcher, 2006). These gels were also effective in preventing the separation of TiO_2 and ZnO in the formulation. The improved stability was ascribed to a stronger internal structure, which is an inherent of the rheological benefits provided by the OCs.

Current concerns about sunscreens include the potential transdermal absorption of chemical UV filters, as well as issues related to skin

phototoxicity and photosensitization (Gubitosa et al., 2020). The use of OCs can address these concerns by adsorbing chemical UV filters, thereby minimizing their dermal migration without compromising effectiveness. For instance, a benzylidene camphor derivative intercalated in Na-Bentonite gives rise to an organomodified bentonite with acquired sunscreen activity (Villa et al., 2015). Similarly, the intercalation of avobenzone and ethyl-hexyl-methoxycinnamate in organophilic bentonite has been shown to prevent or reduced some of the intrinsic side effects of the chemical filters, such as skin irritation and phototoxicity (Dornelas et al., 2015).These modifications highlight the potential of OCs to enhance the safety and efficacy of sunscreen formulations.

3.5. Organoclays in decorative cosmetics

Decorative cosmetics or "make-up" (including lipstick, eyeshadow, mascara, foundation, blush, and nail polish) are applied to the face or body to enhance appearance or cover up defects (Riley, 2000). Usually, these products provide color, texture, or exert various aesthetic effects without claiming therapeutic or medicinal benefits.

Originating in the Middle East 5000 years ago, the globalization and culture changes has spread make-up use, thus becoming a routine. This evolution has driven the cosmetic industry to change and evolve, not only in terms of marketing but also in R&I. This innovation is currently evidenced by multifunctional make-up products: foundations with high SPF, mascaras to lengthen, hydrate, curve and induce lashes growth or long-lasting products such as nail polishes, lipsticks, eyeshadows (Moraes and Vieira, 2020). Since color is one of their fundamental features, remarkable innovation has also been made in this matter (e.g. pigments with specular, duo or multi-chrome effects) (Korichi and Tranchant, 2009). It is worth noting that most pigments are hydrophilic, though hydrophobic pigments must also be considered when formulating make-up.

The roles of OCs in decorative cosmetics are similar to those already mentioned. In products with a lipo-wax matrix (lipsticks, lip-glosses, eye shadows, foundations) the pigments are dispersed in a wax-oil phase, and the gelling agents (i.e. OC) act as stabilizers, preventing pigment sedimentation and other alterations caused by temperature or syneresis. Moreover, they contribute to the final texture by providing creaminess and pleasant application. Depending on the type and oil-gelling agent ratio used it is possible to control the final consistency (viscosity) as well as the color (from transparent to opaque oleogels). Bentonite-based OCs (especially in paste-gel formulas) are among the most widely used gellants in decorative cosmetics (Table 1).

Pigments can also be chemically stabilized by clay minerals.

Anthocyanins are water-soluble, natural polyphenolic pigments with antioxidant activity. They are considered non-polluting pigments due to their inherent color, safety and biodegradability. Moreover, they can provide additional benefits such as antioxidant, anti-inflammatory or bacteriostatic activities (Rose et al., 2018; Sun et al., 2022). For all these reasons, anthocyanins have a great potential in the new generation of cosmetics. Nevertheless, they are sensitive to pH, light and temperature, their activities profitable only after stabilization. Ribeiro and co-workers demonstrated that anthocyanins extracted from blackberries and grapes can be successfully stabilized in MMT (Ribeiro et al., 2018). Although this study used natural clays, the results can be potentially extended to OCs.

As make-up in general, nail painting is an ancient practice that has been dominated by traditional products like Henna (still used today) or red balsam leaves mixed with alum (China in the 1250s) (André and Baran, 2009). Current nail polishes appeared in the early 1920s and typically consists of a colored liquid with various chemical components that adhere to the nails and dry to a hard finish. The main components of nail lacquers are film formers (nitrocellulose) and film modifiers (to improve nitrocellulose performance), modifying resins, plasticizers (awarding flexibility), and solvents (controlling drying time and "brushability") (Giancola and Schlossman, 2016). Suspending agents, UV absorbers, and pigments, are also present (Table 2).

OCs enter the set of nail polishes as suspending agents, driven by the insolubility of most pigments. Therefore, thixotropic ingredients are a must in nail lacquers (André and Baran, 2009; Giancola and Schlossman, 2016), clearly depicting the role that OCs would play in nail formulations: rheology additives to control flow behavior and facilitate colorants dispersion (Jimenez et al., 2021). This task is accomplished by forming a three-dimensional gel-like network that prevents pigment sedimentation (Fig. 4B).

Optimal rheology is also crucial for consumer acceptance and nail polish performance. By comparing different commercial nail formulas Jimenez and co-workers determined some rheology limiting values (Jimenez et al., 2021). Low viscosities ($\eta \approx 10^{-1}$ Pa·s) are preferred for nail coating and dispensing bottle filling; viscosities around 10^{-3} Pa·s are considered too low, associated with runny formulations and excessive brush dripping. At the other end, $\eta > 10$ Pa·s result in tacky formulations and uneven nail spreading (Jimenez et al., 2021). By modifying the type and concentration of OCs it is possible to tailor the final rheology according to the desired performance.

Nail polishes can be classified according to their solvent (aqueous, non-aqueous) or their film-forming method (simple evaporation and drying or photo-polymerization). In the latter case, UV-curable nail lacquers have gained a great deal of attention in the last years Holešová et al., 2013. OCs are also starting to enter this realm.

MMT-CTMA was studied as additive of UV-curable polymers

Table 1
Ingredients used in anhydrous Mascara and their typical concentration range. Modified from Sinha Ray and Okamoto, 2003.

Ingredient role	Common ingredients used	Conc. (wt%)
Solvents	Branched chain hydrocarbons and petroleum distillates, isoparaffinic hydrocarbons, and volatile silicones	40-60
Waxes	Beeswax and its derivatives, candelilla, carnauba, paraffin, polyethylene, microcrystalline, castor, synthetic, ceresin, and ozokerite	10-20
Gellants	Stearalkonium Hectorite, quaternium-18 bentonite, quaternium-18 hectorite, metal soaps (Al, Zn stearates)	3-7
Resins	Could be introduced, but do not have to be include aromatic/aliphatic, hydrogenated aromatics, polyterpene, synthetic, rosin, acrylics, and silicones;	3-10
Colorants	Most often utilize a classic iron oxide without any surface treatment	5-15
Functional Fillers	Spherical particles (PMMA, silica, nylon), boron nitride, starches, Teflon	2-10

Table 2
List of basic ingredients used in nail polish and their typical concentration range.

Ingredient role	Common ingredients used	Conc. (wt%)
Film-Formers	Nitrocellulose	5-15
Plasticizers	Styrene/Acrylates Copolymer, Tosylamide/Formaldehyde Resin, Tosylamide/Epoxy Resin, Acetyl Tributyl Citrate, Trimethyl Pentanyl Diisobutyrate, Triphenyl Phosphate, Ethyl Tosylamide, Camphor, Trimethylpentanediyl Dibenzoate.	4-20
Suspension Agents	Stearalkonium Bentonite, Stearalkonium Hectorite, Silica	0,1-2
Solvents	Ethyl Acetate, Butyl Acetate, Isopropyl Alcohol	1-5
Colorants and Pearls	Titanium Dioxide, Mica, Alumina, Synthetic Fluorphlogopite, Iron Oxides, Calcium Aluminum Borosilicate, Aluminum Calcium Sodium Silicate, Calcium Sodium Borosilicate	65-75
Other additives	Benzophenone-1, Dimethicone	0.001-1

demonstrating to improve the thermal and mechanical properties (Young's modulus) due to clay tactoids intercalated morphology (Uhl et al., 2004), a transferable result for the preparation of decorative cosmetics such as UV-curing nail lacquers (Grigale-Sorocina et al., 2016). Recently, Grigale and Birks studied the impact of Tixogel VZV®, Tixogel LGM®, and Bentone 27 V® as thixotropic agents combined with photocurable urethane dimethacrylate, urethane diacrylate and tetrahydrofurfuryl acrylate polymers. Their influence on the viscosity and stability of the pigments in suspension and on the characteristics of the final film formed was evaluated. After 4 weeks of stability tests (40 °C), synerisis and pigment sedimentation were only prevented in formulations with ≥2 % w/w OC (Grigale-Sorocina and Birks, 2019).

The performance of organoclays in some decorative cosmetics can be jeopardized by their intrinsic color (from brown, yellowish to red), usually associated with impurities such as oxides and hydroxides ion, among others. The natural color of the clay could interfere with the final color of the cosmetic, introducing an undesirable undertone or complicating the achievement of the desired shade. Furthermore, it should be noted that the appearance changes significantly depending on whether the clay is in dry powder form or dispersed in a liquid medium. Dioctadecyldimethylammonium chloride has been used to organomodify a purified bentonite by ion exchange process (Nag et al., 2022). These authors focused their attention on the final appearance of their purified pristine and organomodified bentonite, revealing 81 and 87 % of Hunter whiteness, respectively (Fig. 5A and B). These values were rather close to titanium dioxide (90 %) used as a reference. Based on these results, the final appearance of a purified bentonite can be further improved by organomodification. Moreover, this organoclay maintained its white appearance after casting and liquid dispersion (Fig. 5C and D), unlike other commercially available bentonites (N400) used as control (Nag et al., 2022).

3.6. Safety of organoclays in cosmetics

The production and commercialization of safe cosmetics constitute a key aspect for the European cosmetic regulations. The presence of OCs in cosmetics have arisen some doubts about their safety, even if their natural counterparts are historically considered as safe.

Cloisite® 30B was evaluated for its biocompatibility in vitro and in vivo (Sharma et al., 2010, 2014). According to technical information, Cloisite® 30B contains methyl, bis-2-hydroxyethyl, and C14–C18 alkyl side-chains (tallow) in different proportions. The in vitro studies reported that Cloisite® 30B, suspended in cell culture, was moderately genotoxic to Caco-2 cells, contrary to its counterpart Cloisite® Na. The fact that both filtered and un-filtered Cloisite® 30B were genotoxic led authors to ascribe this effect to the quaternary ammonium salts (Sharma et al., 2010).

The potential exposure to organoclays from oral, pulmonary or transdermal delivery encouraged Han and co-workers to evaluate the in vitro cytotoxicity of a Ca and Mg clay organomodified with APTES (Han et al., 2011). CCD-986sk (normal fibroblasts), A549 (epithelial lung, carcinoma), MRC-5 (normal lung fibroblasts) and HT-29 (colon epithelial carcinoma) cell lines were tested through MTT and Lactate Dehydrogenase tests (Han et al., 2011). Any of the two clays was cytotoxic at concentrations lower than 500 μg/mL. At higher concentrations (1000 μg/mL) the toxicity "was not severe" and appeared to be non-cell specific. Moreover, this concentration did not induce cell apoptosis (Han et al., 2011). The reduction in cell viability by clay minerals in a concentration dependent manner has been widely reported in the literature (Salcedo et al., 2012; Janer et al., 2014; García-Villén et al., 2020a, 2020b). It has been hypothesized that high-concentrated clay suspensions could block cell membrane channels upon sedimentation, thus explaining the lower viability. The same could be happening for OC during in vitro tests. Di-hydrogenated tallow ammonium and dimethyl benzyl hydrogenated tallow ammonium were used to organomodify MMT (Janer et al., 2014). Five cancerous cell lines (Ramos, A549, HCT116, SK-MEL 28, HepG2) and HUVEC were subjected to sonicated OC nanoparticles and media. Again, results pointed out that the organic modifiers were the responsible for cell toxicity (Janer et al., 2014). Other studies reported that octadecyl amine-MMT was cytotoxic for L929 fibroblasts and DLD-1 cancer cells (Rzayev et al., 2017). This work was focused in finding a composite with anti-cancer activity, but the results of the octadecyl amine-MMT were not compared with natural MMT and no other control is included, which makes difficult to determine the real cytotoxicity degree of the studied OCs.

On the other hand, there are also studies reporting that some of the
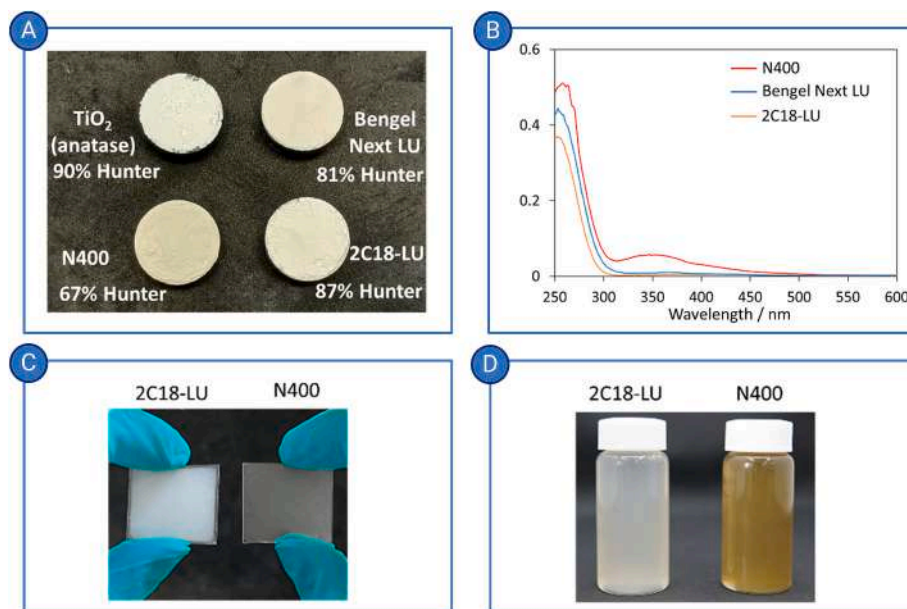
Fig. 5. A) Appearances of the purified, organomodified bentonite (2C18-LU) with respect to a commercial sample (N400) and TiO$_2$ as the whiteness reference. B) UV–vis diffuse reflectance spectra. C) Comparison between films formed by purified bentonite and commercial reference (N400) after casting on a glass surface. D) Color appearance of toluene dispersion (5 % w/w) of purified and organomodified bentonite (2C18-LU) vs commercial sample. Adapted with permission from (Nag et al., 2022). Copyright 2022. American Chemical Society.

most frequently used OCs can be considered as safe. The safety of dis-teardimonium hectorite, dihydrogenated tallow benzylmonium hector-ite, stearalkonium hectorite, and quaternium-18 hectorite was evaluated by Becker and co-workers (Becker et al., 2013). The in vivo studies about Cloisite® 30B genotoxicity and inflammatory potential were conducted by Sharma's research group years later (Sharma et al., 2014). No in-flammatory cytokine markers were found in Wistar rats blood. More-over, no signs of DNA strand-breaks in liver, kidney nor colon cell were detected (Sharma et al., 2014). After reviewing the information avail-able, both in vitro and in vivo, authors concluded that the studied OCs were safe for the current practices.

Most of the existing scientific studies on OCs safety belong to the food packaging industry, where OCs are frequently used. The reviewed studies on this matter will be discussed in the following section, the results possibly extended to cosmetic and personal care product packaging.

4. Organoclays in cosmetic packaging

The growth of the cosmetic industry is not only accompanied by an intense R&I, but also by significant waste generation and pollution. The beauty industry is estimated to generate nearly 120 billion packaging units annually, which is for approximately 40 % of total plastic pro-duction. Furthermore, the plastic used in decorative cosmetic packaging is often non-recyclable due to the contamination by residues from greasy and creamy products and have small, intricate dimensions of the pack-ages, complicating the cleaning process required for recycling (Cinelli et al., 2019; Coltelli et al., 2023).

In response to these challenges, research efforts are increasingly focused on modifying or creating bio-based and biodegradable poly-mers. Examples include poly(lactic acid) (PLA), polyhydroxyalkanoates, and polysaccharides such as nanocellulose. Other natural polymers like chitosan and chitin are gaining attention due to their antibacterial properties, which could improve cosmetic preservation, reduce the ne-cessity of other preservatives as well as exert positive effects over the skin (regenerative and proliferative effects) (Ibrahim et al., 2021). Nevertheless, most of biodegradable polymers do not possess adequate physicochemical and mechanical properties for packaging production, thus needing to be reinforced or formulated with degradable or non-polluting additives. This is the tipping point where clay minerals have proven to be of help.

The role of clays as polymer reinforcers is widely known and appli-cable in many areas. The incorporation of clays and OCs in polymeric matrices has demonstrated to confer strength, controlled gas and water permeability, increased thermal stability (flame-retardant features) (Sinha Ray and Okamoto, 2003; Connolly et al., 2019b) and tailor polymer degradation rate (Cinelli et al., 2019).

Natural clays are hydrophilic, while polymers (especially those used for fabrication purposes) are hydrophobic, making difficult for them to mix properly. In this sense, OCs offer a clear advantage. The interlayer space of layered OCs is higher compared to natural clays (Fig. 1A), making it easier for hydrophobic polymers to intercalate (as outlined in Fig. 3A). In other words, for the formation of OCs/polymer nano-composites, effective polymer intercalation inside the interlayer clay space is of upmost importance (sometimes leading to clay exfoliation, Fig. 6A) (Sinha Ray and Okamoto, 2003). In that review, most of the studies correlated polymer intercalation or clay exfoliation with better mechanical properties. The OCs/polymer hybridization creates new polymer-based materials (OCs/polymer nanocomposites) (Sinha Ray and Okamoto, 2003; Ghadiri et al., 2015; Goyal and Jerold, 2023). The combination of OCs with thermoplastic polymers for packaging pro-duction has been widely studied. Some cosmetic packaging studies have been gathered in this section, though they are still scarce. For this reason, they have been complemented with food packaging studies, whose results are potentially transferable to cosmetic packaging pro-duction. The ultimate goal is to shed some light on the ingredients and key factors to consider.

Two organomodified MMT (hexadecyl trimethyl ammonium bro-mide (HDTA) and acetylcholine) were combined with PLA to produce food-contact bottles through extrusion. The final clay polarity changes according to the alyk ammonium salt used, thus tunning the clay-polymer interactions. HDTA-MMT demonstrated the best barrier and thermal performance (Jorda-Beneyto et al., 2014). Similarly, a high oxygen barrier cosmetic packaging based on perchloroethylene resin and epoxy resin reported the use of OCs, the resultant packaging guar-anteeing high stability and prolonged shelf life (Gu, 2016).

Poly(glycidyl methacrylate) (PGMA)-MMT OCs and TiO_2 were combined with ethylene-vinyl acetate copolymer (EVA) (Bartolomei et al., 2020). Clay organomodification yielded better dispersion within the EVA matrix. PGMA-MMT/EVA composite showed lower tensile strength (Fig. 6B) than MMT/EVA (non-organomodified clay/polymer composite) but the elastic modulus was improved due to higher nano-filler and matrix boding. On the other hand, grafted TiO_2 combined with EVA yields a material with UV absorption capacity (Bartolomei et al., 2020). Consequently, the contemporaneous combination of organo-modified TiO_2 and MMT OCs with EVA (or other thermoplastics) offers a great potential not only for cosmetic packaging, but also for food and medicines.
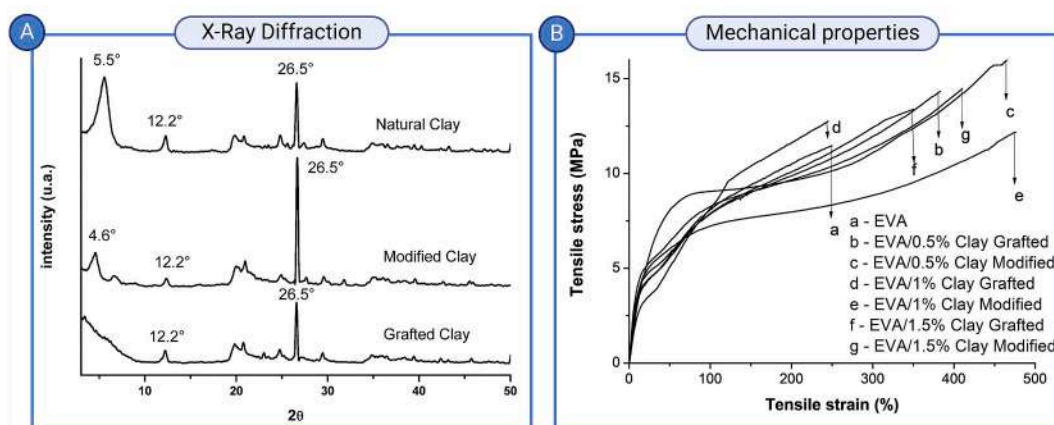
Fig. 6. A) XRD patterns of the clay mineral used by Bartolomei and co-workers. "Natural Clay": pristine MMT clay; "Modified Clay": quaternary ammonium salt MMT; MMT-PGMA is "Grafted Clay". The shifting of 5.5° 2θ towards lower angles (4.6° 2θ (modified clay) confirms organomodification. The disappearance of this reflection in grafted sample indicates clay exfoliation, as represented in (Fig. 3A). B) Tensile stress vs tensile strain curves for raw EVA and MMT/EVA composites ("EVA/Clay Grafted") and PGMA-MMT/EVA composites ("EVA/Clay Modified" in the original graphic). Reproduced with permission from (Bartolomei et al., 2020).

Poly(methyl methacrylate) (PMMA), poly(vinyl chloride) (PVC), poly(vinyl acetate) (PVAc) and natural cellulose acetate butyrate (CAB) thermoplastic polymers were combined with CTAB-MMT (Sudhakar et al., 2021). The tensile strength of all the polymers increased with an increase on CTAB-MMT concentration up to a critical point. Additionally, the polymer degradation was also improved by the presence of OCs.

PLA is one of the most used polymers for packaging purposes. By itself, PLA has good potential as rigid packaging. However, its brittleness, cost, and poor gas barrier properties limit its use (Cinelli et al., 2019). In general, the synthesis of OCs/PLA nanocomposites can help in overcoming PLA drawbacks and improve its performance in biodegradable packaging (Goyal and Jerold, 2023). Two Brazilian MMT (Bofe and Chocolate) were used and compared to prepare CTAB-MMT for PLA modification (Bezerra Lima et al., 2021). Chocolate clay, constituted by 79 % *w*/w MMT, was rich in iron, while MMT constituted only 39 % of Bofe's sample. This difference could explain the higher
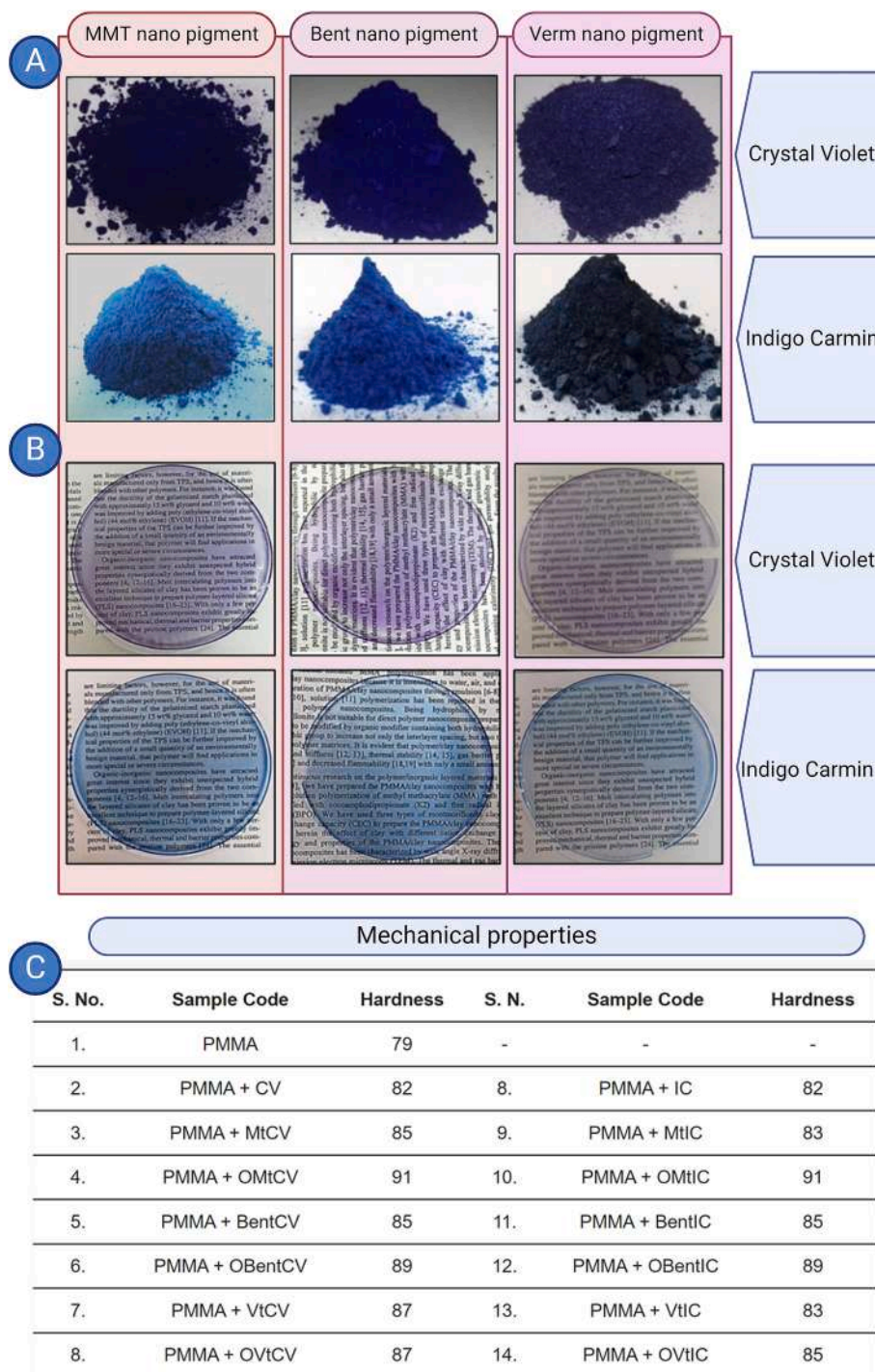

Fig. 7. A) Powder clay based nano pigments. B) Organoclay-based nano pigments dispersed PMMA films. "MMT nano pigment": montmorillonite-based nano pigments; "Bent nano pigment": bentonite-based nano pigments; "Verm nano pigment": vermiculite-based nano pigments. C) Hardness of PMMA films depending on natural clay-based or organoclay-based nano pigments. PMMA: poly (methyl-methacrylate. CV: crystal violet. Mt.: montmorillonite. OMt: organomodified montmorillonite. Bent: bentonite. OBent: organomodified bentonite. Vt: vermiculite. OVt: organomodified vermiculite. IC: indigo carmin. Modified from (Mohan et al., 2023). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

strength of CTAB-Chocolate/PLA with respect to its counterpart and exemplifies the importance of purity assessment in natural clays to maximize their performance. It is also worth noting that STEM-in-SEM images showed some degree of alignment of clay particles during the extrusion process, which can also explain the polymer's mechanical improvement (Bezerra Lima et al., 2021).

Hong and Rhim investigated the antimicrobial properties of Cloisite 20 A and Cloisite 30B in clay/polymer composites, discovering bactericidal effects against *S. aureus, L. monocytogenes, S. typhimurium*, and *E. coli* (Hong and Rhim, 2008). These findings suggest that OCs and polymers combined in packaging materials could offer intrinsic antimicrobial properties, thus potentially reducing the need for additional antimicrobial preservatives in cosmetic products and enhancing consumer appeal (Hong and Rhim, 2008). More recently, a cosmetic packaging bottle coating that claims to have good antibacterial and barrier properties was prepared by mixing chitosan with a layered clay mineral powder formed of kaolin, MMT, and talc (Wang and Tan, 2019).

LDH clays have also had the opportunity to demonstrate their potential. PLA and poly[(butylene succinate)-*co*-adipate (PBSA) mixtures were intercalated with LDH organomodified with surface stearic functional groups to form SaLDH OCs. Different SaLDH concentrations were tested (0.1, 0.5 and 1 % *w/w*), 0.5 % being the most effective one in improving thermal, mechanical and oxygen barrier properties of polymers. Yet another testament to the utility of OCs and their high prospects in the industrial development of environmentally sustainable packaging (Mhlabeni et al., 2019).

As previously stated, organomodification is frequently applied to layered clay minerals. Nevertheless, sepiolite and palygorskite are fibrous phyllosilicates without an interlayer space, their organomodification limited to their surface. Despite that, they are still considered good reinforcing agents and present outstanding absorption capacity, as exemplified by the study of García-Quiles and co-works (García-Quiles et al., 2019).

As part of their evolution, brands also concentrated part of their efforts in developing attractive packaging to draw customer's attention. Recently a new generation of clay-based nanopigments has been introduced. Mohan and *co*-authors proposed the use of clay-based and OCs-based nanopigments for polymer coloring, together with a novel methodology for the synthesis of value-added products (Mohan et al., 2023). Non-biodegradable dyes such as crystal violet and indigo carmin were loaded into MMT, vermiculite, and their organomodified counterparts (Fig. 7A). Cetylpyridinium chloride (CPC) was used for the organomodification through aqueous synthesis. Pristine clay minerals were more prone to adsorb cationic dye (crystal violet), while indigo carmin was retained with more efficiency by OCs. During poly (methyl-methacrylate) (PMMA) coloring, OCs performed better in terms of homogeneous dispersion, awarding more intense color (Fig. 7B). The mechanical properties of the OCs/PMMA colored-polymer were higher than PMMA alone (Mohan et al., 2023) (Fig. 7C). This study opens a new strategy for packaging and circular economy: OCs can be used to adsorb different dyes from wastewater (for instance) and be re-used for polymer reinforcement and coloring in packaging. Notwithstanding this promising proposal, the toxicity of the OCs, the dyes, and their release (if any) must be thoroughly evaluated to guarantee product safety.

Similarly to what occurs in decorative cosmetics, the intrinsic color of clays can affect the final packaging appearance. As demonstrated by Nag et al., prior purification of the mineral can be highly beneficial in this regard (Nag et al., 2022), removing impurities with undesirable hues and allowing the natural white color of the pure mineral to be maximized.

4.1. Safety of organoclays in cosmetic packaging

Due to the proven usefulness of OCs in packaging, some studies addressing their safety are available. Even if some of the studies reported herein are specific for food packaging, they can be transferable to cosmetic packaging, providing a valuable starting point. For example, an HDTA-MMT/PLA composite for bottle fabrication was found cytotoxic for in vitro Caco-2 and HepG2 cells, which is a significant consideration if oral exposure might occur (Jorda-Beneyto et al., 2014). The authors noted that the type and concentration of the organomodification molecules exerts a significant influence in cytotoxicity. In a later study, they focused on studying the cytotoxicity of OC on their own (no clay/polymer composite was prepared). No cytotoxic effects were found for HDTA-MMT over HUVEC cells, although it exhibited potential mutagenicity in TA98 *Salmonella typhimurium* strain. HDTA/acethylcholine chloride-MMT clay produced cytotoxicity in HUVEC but no mutagenicity was recorded. On the other hand, Cloisite® 30B a safer profile in vitro (Maisanaba et al., 2015).

Na-MMT was organomodified with 3-aminopropyltriethoxysilane (APTES) and vinyltrimethoxysilane (VTMS) as polypropylene (PP) nanofillers (Maisanaba et al., 2018). Firstly, the cytotoxicity of APTES-MMT and VTMS-MMT extract was evaluated, showing that APTES-MMT was not cytotoxic for Caco-2 cells. VTMS-MMT started to show cytotoxic effects after 48 h of contact with Caco-2 cells, though cell viability remained >60 % (confirmed by flow cytometry). Then, an APTES-MMT/PP composite was prepared and further evaluated, showing no cytotoxicity and accomplishing the EU regulation on materials for food contact (Maisanaba et al., 2018).

The use of OCs in cosmetic packaging is a recent field of study, reason why their safety assessment is still limited (Goyal and Jerold, 2023). In this regard, potential exposures through mucosa (eye or mouth) and skin must be considered depending on the type of product. The commercial sodium bentonite (Nanofil®116) organomodified with HDTA and octadecyl trimethyl ammonium chloride (TMSA) was studied as PLA reinforcement in cosmetic packaging (Connolly et al., 2019b). The in vitro cytotoxicity results, once again, suggested that the cationic surfactant type and concentration exerts the major difference (Connolly et al., 2019b). In another study, the hazard of migration extracts from OCs/polymer nanocomposites for cosmetic packaging, following dermal exposure, was addressed (Connolly et al., 2019a). Nanofil®116, organomodified with TMSA and HDTA, were combined with PLA and subjected to biocompatibility studies, complemented with component's migration analysis. The overall migration of components from Nanofil® 116-PLA nanocomposites was low and within the permitted levels. No toxicity against HaCaT keratinocytes or the artificial skin model were found, thus concluding that the PLA nanocomposites developed were safe for cosmetic packaging (Connolly et al., 2019a).

On the other end it is possible to find studies that propose OCs to prevent the migration of toxic ingredients from packaging. Polystyrene is one of the most consumed polymers for food packaging. During polymerization, some styrene monomers (considered carcinogenic, toxic for liver, respiratory and cardiovascular system) can remain in the final product, prone to migrate. Cloisite® 15 A and ZnO nanoparticles were evaluated as inhibitors of styrene monomer migration. The diffusion coefficient of styrene monomer decreased with the addition of ZnO and Cloisite® 15 A (50 and 10 % reduction, respectively), though polysterene/ZnO-Cloisite reported the lowest Fickian diffusion coefficient (Abolghasemi-Fakhri et al., 2019).

5. Conclusions

The future prospects for organoclays in the cosmetic and personal care industries are promising, driven by ongoing innovations and advancements in their functionalization, integration with nanotechnology, and expanded applications in environmental and industrial processes. Here are some key points highlighting their potential:

1. Advanced Functionalization and Integration with Nanotechnology: Future developments are expected to focus on enhancing the functional capabilities of organoclays through advanced chemical modifications and integration with nanotechnology. This approach will

lead to the creation of novel multifunctional nanomaterials with improved adsorption abilities and interfacial properties, making them highly valuable in cosmetic formulations.

2. Multifunctional Applications: Organoclays can serve multiple roles in cosmetic products, such as stabilizing emulsions, controlling viscosity, enhancing sensory attributes, and boosting SPF effectiveness in sunscreens. By combining different types of clay minerals and optimizing their organomodification, synergistic effects can be achieved to overcome individual drawbacks and improve overall product performance.

3. Sustainability and Safety: As consumer demand for sustainable and safe ingredients grows, organoclays offer advantages due to their natural origin and eco-friendly profiles. Efforts to modify clay minerals with biosurfactants and other green additives aim to reduce cytotoxicity and microbial proliferation concerns, ensuring their suitability for cosmetic use.

4. Cosmetic Packaging Innovations: Organoclays are also poised to contribute significantly to the evolution of cosmetic packaging. Their ability to enhance barrier properties, mechanical strength, and sustainability aligns with the industry's shift towards eco-conscious packaging solutions. Technologies like 3D printing, enabled by organoclays, could revolutionize the production of personalized and functional cosmetic packaging.

5. Regulatory and Technological Advancements: Over the next five years, advancements in regulatory frameworks and production techniques (such as additive manufacturing) will likely support the broader adoption of organoclays in cosmetics. This includes ensuring their safety and efficacy while meeting evolving consumer preferences for natural and effective ingredients.

6. Overall Outlook: The evolving landscape of cosmetic and personal care products will increasingly rely on organoclays for their versatility, performance benefits, and sustainability credentials. As research continues and technologies evolve, organoclays are set to play an essential role in shaping the future of cosmetic formulations and packaging.

In conclusion, organoclays represent a pivotal ingredient category poised for significant growth and innovation within the cosmetic industry, driven by their unique properties and their alignment with consumer and regulatory trends towards sustainability and safety.

6. Future prospects

The future prospects for OCs in the cosmetic and personal care industries are promising, driven by innovations and advancements in their functionalization, integration with nanotechnology, and expanded applications in environmental remediation and industrial processes. These developments will likely be accompanied by efforts to ensure sustainability, cost-effectiveness, and regulatory compliance, ultimately broadening the impact and utility of organoclays in various sectors.

The future perspective for organoclays in cosmetics and personal care products can foresee the chemical combination of different clay minerals (Massaro et al., 2021) that, at the same time, can be organomodified. This strategy ensures the development of novel multifunctional nanomaterials, with complementary adsorption abilities and improved interfacial properties with respect to pristine clays. The resultant synergic features of these newly "coupled", organomodified clay minerals could ease cosmetic's production (by simplifying formulation) or improve their final performance (by counteracting their respective drawbacks or by complementing their functional roles). Additionally, organomodified synthetic layered polysilicates such as magadiite, ilerite and kenyaite could be promising for future cosmetic applications. The synthetic nature of these minerals (and therefore, intrinsic purity) with the advantages of organomodification could boost the industry of cosmetics and personal care products in the coming years.

Although they are considered sustainable materials, additional concerns about environmental and human safety of organoclays are not only foreseeable, but a current issue to be addressed to guarantee these ingredients can reach their full potential. In this regard, the organomodification of clay minerals with natural, ecofriendly ingredients such as biosurfactants from bacteria and fungi (i.e. surfactin and others) may damper their final cytotoxicity and help in controlling microbial proliferation, both as part of the formulation or the packaging.

In the same line, and considering the strong suit of these minerals, sunscreens will continue to evolve to non-contaminant, sustainable formulations. For instance, the combination of different SPF boosters (organoclays and biological compounds from microorganisms and plants) could lead to synergies, softening the need for synthetic UV filters.

As revealed by this review, OC are not only promising for cosmetic formulations but also for future packaging materials. Their ability to improve barrier properties, mechanical strength, and sustainability aligns well with current industry trends and consumer demands. The aforementioned chemical combination of clay particles (Massaro et al., 2021) could be extensively exploited in this field. In terms of production, the booming and continuous evolution of additive manufacturing techniques such as 3D printing in combination with sustainable, multifunctional ingredients such organoclays, could propel future advances in cosmetic packaging. In fact, 3D printing is a promising production technique for an industry with such a fast development, where brands are somehow constricted to draw consumers attention with details like packaging. 3D printing offers a great versatility to modify the shape and dimensions of the printed structure. Nevertheless, the polymers to be printed must present adequate rheological properties, which could be obtained and modified by natural and organomodified clay minerals. In other words, 3D printing and organoclays are a fundamental combo for the evolution of this area. Additionally, 3D printing and organoclays also enables the production of personalized packaging according to consumer needs and demands. For instance, single doses of certain formulations could provide more reproducible results to consumers (the same, adequate dose is used constantly). Moreover, single dose, personalized packaging will improve stability of formulations containing labile actives or susceptible to microbial contamination, thus increasing safety and reducing preservatives concentration.

Bearing all of this in mind, significant progress is expected over the next five years in the methods of functionalizing organoclays, allowing for more precise control over their properties and safety. The synergy between organoclay and nanotechnology will likely deepen, favouring the development of new hybrid nanomaterials for cosmetic formulations and packaging. Organoclays roles in sustainable production practices will also increase within five years, propelled by the cost production reduction. Collaterally, as the use of organoclays expands, there will likely be a corresponding evolution in regulatory frameworks to ensure their safe and effective use, especially as ingredients of cosmetics and personal care products.

In summary, the future for organoclays in the cosmetic field appears to be quite promising, driven by their unique properties and the increasing demand for natural and sustainable ingredients in personal care products.

CRediT authorship contribution statement

Fátima García-Villén: Writing – original draft, Visualization, Methodology, Investigation, Funding acquisition, Formal analysis. **César Viseras:** Writing – review & editing, Project administration, Funding acquisition, Conceptualization. **Rita Sánchez-Espejo:** Writing – original draft, Investigation, Funding acquisition, Formal analysis. **Serena Riela:** Writing – review & editing, Validation, Supervision. **Marina Massaro:** Writing – review & editing, Visualization, Supervision. **Raquel de Melo Barbosa:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Resources, Project administration.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests.

Data availability

No data was used for the research described in the article.

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