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Review

## Toxicological evaluation of clay minerals and derived nanocomposites: A review



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### ABSTRACT

Clays and clay minerals are widely used in many facets of our society. This review addresses the main clays of each phyllosilicate groups, namely, kaolinite, montmorillonite (Mt) and sepiolite, placing special emphasis on Mt and kaolinite, which are the clays that are more frequently used in food packaging, one of the applications that are currently exhibiting higher development. The improvements in the composite materials obtained from clays and polymeric matrices are remarkable and well known, but the potential toxicological effects of unmodified or modified clay minerals and derived nanocomposites are currently being investigated with increased interest. In this sense, this work focused on a review of the published reports related to the analysis of the toxicological profile of commercial and novel modified clays and derived nanocomposites. An exhaustive review of the main *in vitro* and *in vivo* toxicological studies, antimicrobial activity assessments, and the human and environmental impacts of clays and derived nanocomposites was performed. From the analysis of the scientific literature different conclusions can be derived. Thus, *in vitro* studies suggest that clays in general induce cytotoxicity (with dependence on the clay, concentration, experimental system, etc.) with different underlying mechanisms such as necrosis/apoptosis, oxidative stress or genotoxicity. However, most of *in vivo* experiments performed in rodents showed no clear evidences of systemic toxicity even at doses of 5000 mg/kg. Regarding to humans, pulmonary exposure is the most frequent, and although clays are usually mixed with other minerals, they have been reported to induce pneumoconiosis *per se*. Oral exposure is also common both intentionally and unintentionally. Although they do not show a high toxicity through this pathway, toxic effects could be induced due to the increased or reduced exposure to mineral elements. Finally, there are few studies about the effects of clay minerals on wildlife, with laboratory trials showing contradictory outcomes. Clay minerals have different applications in the environment, thus with a strict control of the concentrations used, they can provide beneficial uses.

Despite the extensive number of reports available, there is also a need of systematic *in vitro*–*in vivo* extrapolation studies, with still scarce information on toxicity biomarkers such as immunomodulatory effects or alteration of the genetic expression. In conclusion, a case by case toxicological evaluation is required taking into account that different clays have their own toxicological profiles, their modification can change this profile, and the potential increase of the human/environmental exposure to clay minerals due to their novel applications.

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### 1. Introduction

Clays and clay minerals (Table 1) belong to the phyllosilicate group (from the Greek “phylon”: leaf, and from the Latin “silic”: flint) (Fig. 1). As a distinctive feature, these materials are very small (a few micrometres maximum), and their preferred formation occurs under the surface (alterites, soils, and sediments) or

subsurface (diagenesis and hydrothermal alterations) conditions (Meunier, 2005). The physical and chemical properties of a particular clay mineral are dependent on its structure and composition. The structure and composition of the main industrial clays, *i.e.*, kaolins (1:1 phyllosilicates), smectites (2:1 phyllosilicates) and sepiolite (2:1 inverted ribbons), are very different (Table 2), even though each is composed of octahedral and tetrahedral sheets as their basic building blocks. However, the arrangement and composition of the octahedral and tetrahedral sheets account for most of the differences in their physical and chemical properties (Murray, 2007a).

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Table 1  
Differences between clay and clay mineral (Bergaya and Lagaly, 2013).

Clay	Clay mineral
Natural	Natural and synthetic
Fine-grained (< 2 or < 4 μm)	No size criterion
Phyllosilicates as principal constituents	May include non-phyllosilicates
Plastic (with some exceptions like flint clays)	Plastic
Hardens on drying or firing	Hardens on drying or firing

Clays and clay minerals, either as such or after modification, are recognized as the materials of the 21st century because they are abundant, inexpensive and environmentally friendly. Further introductory aspects of clays have been described by Bergaya and Lagaly (2013). Phyllosilicates are very important industrial minerals. There are well over 100 documented industrial applications of clay materials. Clays are utilized in the process industries, in agricultural applications, in engineering and construction applications, in environmental remediation, in geology, and in many other miscellaneous applications (Murray, 2007b). Currently, the use of several clays in the food industry is a reality for improving food packaging. This review focused on the main clays of each phyllosilicate group, namely kaolinite, montmorillonite (Mt) and sepiolite, and placed special emphasis on Mt and kaolinite, which are the clays that are more frequently used in food packaging.

These two clay minerals are among the most frequently used solid fillers for obtaining novel polymer composites, named nanocomposites, due to the small quantity of clay minerals that is added to the polymer matrix to control the final properties of the nanocomposite and to yield better workability (Annabi-Bergaya 2008; Arora and Padua, 2010). The octahedral and tetrahedral sheets of their structure, which are known as platelets, are approximately 1 nm thick and 100 to 500 nm in diameter, resulting in platelets with a high aspect ratio (Uyama et al., 2003), but clays are formed by numerous platelets, yielding submicrometer particles. When clays are dispersed into a polymer matrix, they experience swelling, dividing all of the platelets into independent units at the nanometre scale, hence the name “nanocomposite materials”. These platelets force gases to follow a tortuous path through the material which greatly slows their transmission. As a result, a nanolayer clay structure is obtained, and the path of diffusion of the penetrating molecules of gases and other substances increases, providing substantially improved products (Abacha et al., 2009; Choudalakis and Gotsis, 2009; Herrera-Alonso et al., 2010). The effect of nanoclays on the polymer properties lies mainly on their high surface-to-volume ratio because polymer–filler interactions are governed by interfacial forces (Arora and

Padua, 2010). The successful formation of a polymer–clay nanocomposite relies on two key characteristics of the component used for reinforcement. The first characteristic is the ability to modify the chemical surface of the silicates through ion-exchange reactions with organic and inorganic cations in order to produce a polymer-compatible nanocomponent. The second characteristic is the ability of the silicate particles to disperse into the polymer, yielding an exfoliated nanocomposite. In this regard, three different clay dispositions can be obtained: (1) Tactoid structures remain in a polymer when the interlayer space of the clay gallery does not expand, usually due to its poor affinity with the polymer. No true nanocomposites are formed this way (Alexandre and Dubois, 2000). (2) Intercalated structures are obtained at moderate expansion of the clay interlayer. In this case, interlayer spaces expand slightly as polymer chains penetrate the basal spacing of clay, but the shape of the layered stack remains. This is the result of moderate affinity between polymer and clay. (3) Exfoliated structures, clay clusters lose their layered identity and are well separated into single sheets within the continuous polymer phase. This is due to a high affinity between polymer and clay (Arora and Padua, 2010) (Fig. 2). These two characteristics are, of course, connected to each other because the degree of dispersion of a layered silicate in a particular polymer matrix depends on the interlayer cation modification (Ray and Okamoto, 2003). However, a simple dispersion of clays in a polymer matrix will not produce a nanocomposite with better properties compared with those of the bulk material due to the poor interfacial interactions between the hydrophilic reaction sites of clays and the highly hydrophobic polymer chains (Pisticelli et al., 2010). The solution for the aforementioned disadvantages can be achieved by introducing organic groups to enhance the interaction between the clays and polymers (Silva et al., 2011). In this sense, cation exchange is one of the most useful chemical modification procedures used to prepare more organophilic clays (Pavlidou and Pappaspyrides, 2008; Paul and Robenson, 2008; Ray and Okamoto, 2003), and one of the modifiers that is most frequently used is quaternary ammonium salts (Fig. 3). This produces modified clays with a hydrophobic character and a greater interlayer space (Betega de Paiva et al., 2008; Jordá-Beneyto et al., 2014). Several quaternary ammonium salt-modified clays are available in the market, and other clays are under development; thus, all of these result in recognized improvements to the polymers (Bin-Haron, 2010; Carreu, 2011; Jordá-Beneyto et al., 2014; Lai and Kim, 2005; Pal et al., 2014).

Although the beneficial technical effects of the nanocomposites obtained from clay minerals have been known for years and are generally well described, the potential toxicological effects and impacts of unmodified or modified clay minerals and derived nanocomposites on human and environmental health are

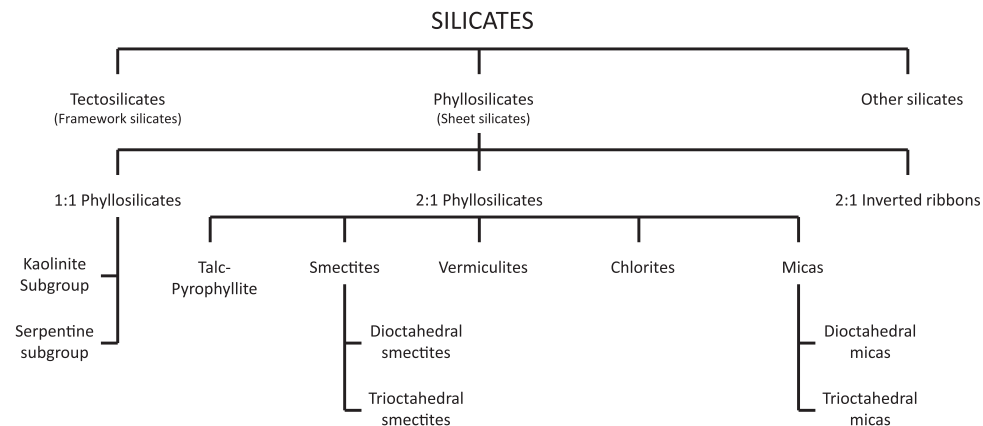


Fig. 1. Classification of silicates with the main subgroups of clays (WHO, 2005).

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