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Research Article

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Characterization of intercalation compounds of sunscreens in a bentonite organoclay

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ABSTRACT

Sunlight, especially UV radiation, is known forits beneficial effects, but even more for its harmful ones. As a result, the use of sunscreen preparations have been growing recently, which has led to their efficacy and safety being a current topic of investigation. The aim of this work was to obtain intercalation compounds of UVA avobenzone (AVO) and UVB ethylhexylmethoxycinnamate(EHMC) sunscreens and an organophilicbentonite (OB), in which the sunscreens were chosen because of the problems associated with their use, and the clay for its already described capacity to act as a physical sunscreen. The intercalation compounds (AVO-OB and EHMC-OB) were obtained by a solution technique and characterized using transmission electronic microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), powder X-ray diffraction (XRPD) and thermal analyses (TG/DSC). The basal spacing data of OB was maintained in both. Furthermore, the TEM micrographs of both corroborate the XRPD results. Thermal analysis confirmed the formation of intercalation compounds with the disappearance of the melting point peaks of the sunscreens. Moreover, the concentrations of sunscreens in AVO-OB and EHMC-OB were quantified, at around 1% and 3%, respectively. These data account for the FTIR bands of the guest molecule overlapping those of the clay. All these findings demonstrated the intercalation, in a simple process, of AVO or EHMC in the layered structure of bentonite. The investigation of these nanocomposite systems on the preservation of the sunscreen properties in order to enhance the SPF and avoid sunscreen contact with the skin are our next steps.

Keywords: Avobenzone; ethylhexylmethoxycinnamate; intercalation compounds; layered clay; sunscreen.

INTRODUCTION

UV radiation is classified according to the range of wavelengths in UVA (UVA1, 400-340 nm and UVA2, 340-320 nm), UVB (320-290 nm) and UVC (290-100 nm), which is an electromagnetic radiation responsible for most of the beneficial to healthy, but which also has harmful side effects for human beings. UVA region radiation is able to penetrate the skin with greater intensity causing premature ageing, while UVB frequencies are largely absorbed by the outer layers of the skin. However, the latter have been shown to cause direct photoactivation of the DNA molecule, producing mutagenesis and carcinogenesis. In general, UV radiation causes a variety of molecular changes that lead to immunosuppression. UV-C is usually absorbed by the ozone layer in the atmosphere[1-4].Although human beings have developed several mechanisms to protect themselves against sun radiation, these are not sufficient and skin photoprotection using safe sunscreen preparations has become highly desirable.

The usual approach to providing higher sun protection factor (SPF) in sunscreen preparations is the association of organic and/or inorganic synthetic filters. However, skin irritation, phototoxic reactions and photoallergy may occur after the use of sunscreen. One approach to reducing skin reactions is the use of molecules based on natural resources such as layered clays, which are able to form intercalation compounds with sunscreens. As previously reported, sepiolite and smectites were used to form complexes with the solar filters ethyl cinnamate and N-methyl 8-hydroxy quinolone methyl sulfate[5-7]. Oxybenzone (OXB) intercalated into zeolite demonstrated that the protective properties of OXB are preserved[8]. Perioli *et al.*[9]intercalated the sunscreen 2-phenyl-1H-benzimidazole-5-sulfonic acid (Eusolex 232, EUS)into hydrotalcite. The results showed that this clay is a good matrix for sunscreen formulations, avoiding problems related to sunscreens such as photodegradation and photoallergies. Moreover, these intercalation compounds maintained the properties of sunscreens. In addition, Hoang-Minh *et al.*[10]reported that clays present the ability to afford protection agains tUV radiation through absorption or reflection. In this study, different mean UV-transmission values were found for various clays incorporated into creams, indicating that clays can absorb UV radiation by themselves, without any additives.

Bentonite is the most common member of the smectite clay family, which is sometimes referred to as ‘‘nanoclay’’, or “nano-montmorillonite” (its major component), and belongs to the general mineral group of layered clays, the shape of whose particles is that of sheets firmly arranged in structural layers, which are much longer and wider than the thickness[11].The layer is a unit consisting of an alumina octahedral sheet (O) sandwiched between two silica tetrahedral sheets (T), i.e. TOT layers. Isomorphous substitution within the silicate layers is responsible for the presence of exchangeable cations within the interlamellar region and confers its swelling capacity in water. However, the replacement of the inorganic cations in montmorillonite by organic cations, e.g. alkylammonium, leading to organoclays, is known to cause considerable modifications inthe hydration and swelling properties of the clay[12].

In this way, the layered structured nanocomposites formed by clay and sunscreens incorporated into sunblocks have two main advantages: i) to protect sunscreens against direct sun radiation, increasing their photostability and promoting prolonged effects on the skin; ii) to avoid the direct contact of sunscreens with the skin.

Based on these findings, the present study deals with the intercalation of the usual UVA and UVB sunscreens, avobenzone(AVO) and ethylhexylmethoxycinnamate(EHMC), in an organophilic layered structured bentonite. The physicochemical characterization of the intercalation compounds was also carried out.

EXPERIMENTAL SECTION

Materials

Organophilicbentonite (OB) modified with octadecylamine salt(Viscogel B8®) was purchased from Bentec (Livorno, Italy). 1-(4-Methoxyphenyl)-3-(4-*tert*-butylphenyl)propane-1,3-dione,known as avobenzone (AVO), a solidlipophilic UVA sunscreen, and (*RS*)-2-ethylhexyl (2*E*)-3-(4-methoxyphenyl)prop-2-enoate, known as ethylhexylmethoxycinnamate(EHMC), an oil UVB absorber sunscreen, were provided by Fagron (São Paulo, Brazil). Ethanol reagent grade was furnished by Merck (Darmstadt, Germany).

Preparation of sunscreen-bentonite intercalation compounds

The intercalation compounds were prepared using a solution technique. The sunscreen was initially dissolved in ethanol and the bentonite was added at different weight ratios, under vigorous stirring for 2 hours, to form intercalation compounds named AVO-OB and EHMC-OB. Next, the dispersion was centrifuged at 4000 rpm (KR-20000T centrifuge laboratory, Kubota, Tokyo, Japan) for 15 min, and the pellets were set side for characterization.

Characterization of sunscreen-bentonite intercalation compounds

X-ray powder diffraction (XRPD) data were obtained from a PW 1710 Philips diffractometer using Cu Kα radiation at 30 mA, 30 kV. Patterns were recorded over the 2θ range 2 to 40^o in steps of 0.02^o with a count time of 2 s. The d-spacing was calculated using Bragg’s equation. Transmission electron microscopy (TEM) measurements were performed using a TECNAI 20 microscope (FEI, Tokyo, Japan). The sample was dispersed in ethanol under mechanical stirring before spreading on the surface of carbon grids. Infrared spectra were recorded on a Bruker Vertex 70 Fourier transform spectrometer (BrukerOptik, Ettlingen, Germany). Samples were measured over a wavelength range from 650 to 4000 cm^{-1} using an attenuated total reflectance (ATR) accessory. Simultaneous TG/DSC measurements of 5-mg samples placed in aluminum crucibles were carried out in a thermoanalizer (STA 449 F1 Jupiter, Netzsch, Selb, Germany) from 25 to 500^o C with a heating rate of 10 °C min^{-1} in an inert nitrogen flow.

RESULTS AND DISCUSSION

X-ray powder diffraction. XRPD patterns of 2:1 AVO-OB and 0.5:1 EHMC-OB intercalation compounds are shown in Figure 1. OB diffractogram(Figure 1a) shows a peak at 29.25 Å recorded at low diffraction angles, which corresponds to the basal spacing d_{001} according to Bragg´s equation. This value, higher than that of bentonite, about 11 Å[13], is justified by the presence of the organic cation in the interlayer space. No differences in d_{001} values were found for neither the AVO-OB nor the EHMC-OB intercalation compounds (Figures 1b and 1c). In the case of OB ,a secondary molecule adsorption, since the primary is with the alkylammonium, may result in a lack of expansion of the interlayer space, irrespective of the occurrence of a compound intercalation. In fact, the swelling of the alkylammonium derivatives in polar solvents, such as ethanol, was analyzed based on the formation of solvent clusters (pores) between the alkyl chains. These pores between alkyl chains can be occupied by many polar organic molecules. The long amine chains were dissolved into oil or other hydrocarbon droplets, holding or fixing them due to electrostatic and van der Waals forces[14, 15].

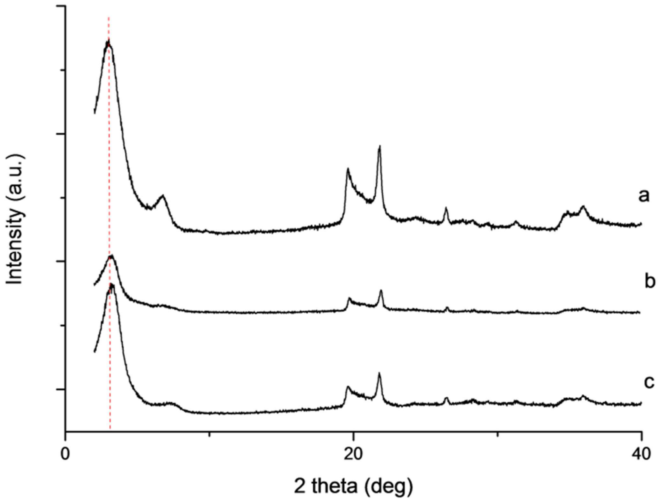

Figure 1.Powder X-ray diffractograms of OB (a); AVO-OB (b); EHMC-OB (c)

Transmission electronic microscopy. The maintenance of the OB layered structure in the sunscreen-bentonite intercalation compounds is evidenced by the regularly aligned lines shown in the TEM micrographs (Figure 2). The measured interlayer distance was about 3 nm, which is in agreement with the XRPD findings. It should be noted that the distance between the clay layers is maintained constant in a well-organized form and no sunscreen agglomerated structures were observed in any of the intercalation compounds. These data suggest that the sunscreen molecules are well packed between the bentonite layers.

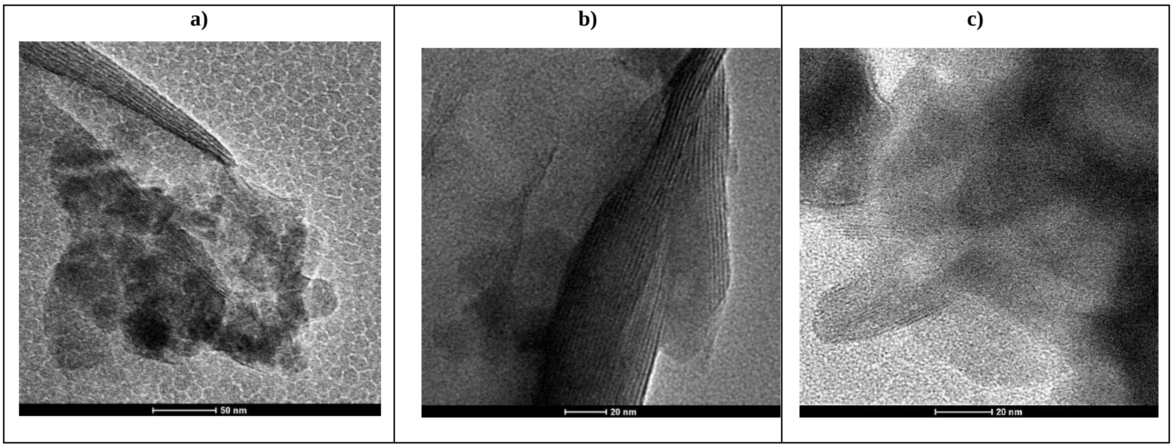

Figure 2. TEM images of OB (a); AVO-OB (b) and EHMC-OB (c)

Thermal analysis. DSC thermogram of OB showed a discrete endothermic peak at around 100 °C (Figure3a)and may be ascribed to the residual water molecules, which are physisorbed in the interparticle pores of the clay [15]. A mass loss of 1.14% was calculated. Moreover, an endothermic peak at 404 ^{o}C (onset) was observed, probably related

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to the OB alkylammonium groups. In addition, a continuous mass loss of 30.56% since200 ^{o}C was found, associated with the gradual decomposition of the organic molecule and dehydroxylation of lattice water, which is accompanied by the decomposition of the external clay components, as reported by Tabak *et al.*[16].The DTG curve (Figure3b) shows that the decomposition process of OB is mainly determined by two events with inflection points at around 330 and 405 ^{o}C.

The TG/DTG curves of AVO present two stages of the weight loss process, starting at around 300 ^{o}C with inflection points at 405 ^{o}C (85.9%) and 440 ^{o}C (6.8%) (Figure3b). An endothermic peak with onset at 83.3 ^{o}C (ΔH: 66.8 J/g) was found (Figure3a), corresponding to the melting event, followed by a complex process of decomposition from ~330 ^{o}C, as reported by Nesseem[17]. The melting peak disappeared in the AVO-OB intercalation compounds, but the decomposition process was still observed, confirming the presence of AVO in the intercalation compound. This is confirmed by comparing the DTG curves, as the peaks corresponding to AVO and OB overlapped in the AVO-OB intercalation compounds. Despite this, there is an overlapping of the decomposition events of AVO and OB at around 405 ^{o}C, Figure3b shows that the main contribution to the mass loss (17%) results from an event at 348 ^{o}C.

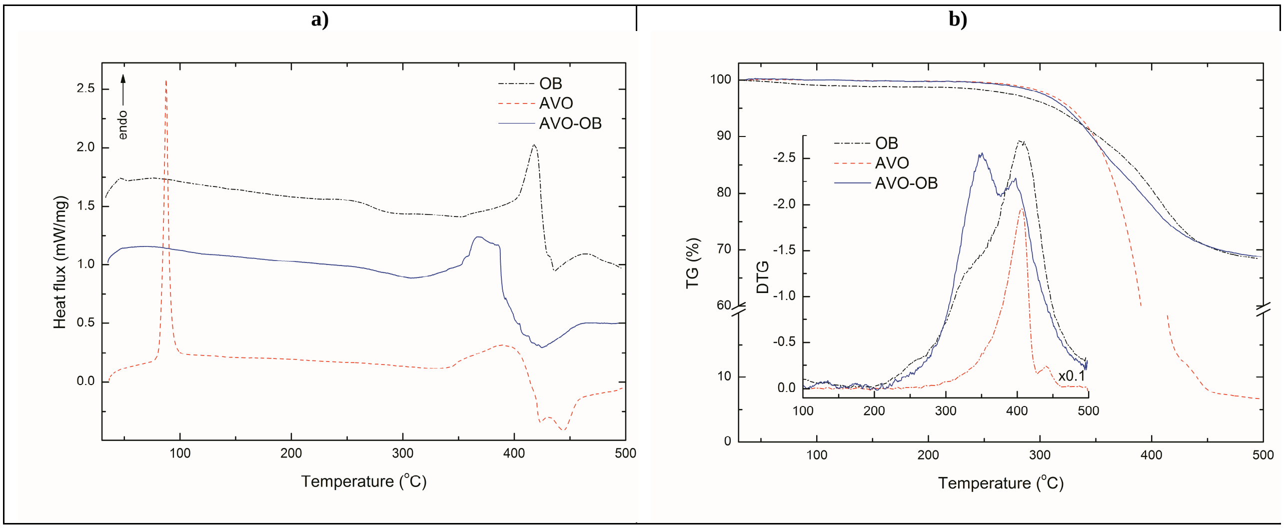

Figure 3.DSC (a) and TG/DTG (b) curves of AVO

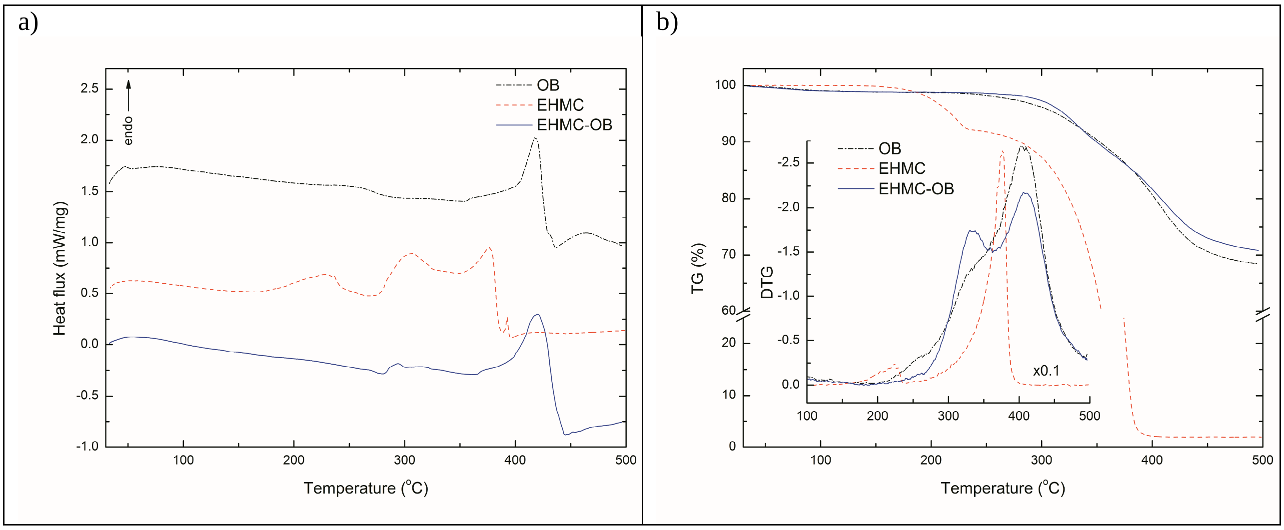

Figure 4.DSC (a) and TG/DTG (b) curves of EHMC

The DSC curve of EHMC presents a broad peak (onset: 179.9 ^{o}C, ΔH: 47.1 J/g), ascribed to the melting point (Figure4a), which has an associated mass loss of 8.1 %. A second decomposition event, corresponding to a mass loss of 90.0%, is related to a complex thermal behavior signature. EHMC degrades almost completely below 500 ^{o}C, as previously reported[18].The DSC curve of EHMC-OB is very similar to that of pure EHMC and OB, but the stage of weight loss related to the EHMC melting point disappeared. This confirms the formation of an intercalation compound, suggesting that non-unreacted EHMC molecules were present in the product. The presence of the EHMC-OB intercalation compound was also observed in the DTG curve (Figure 4b), with the increase in the peak at 333 °C.

Finally, considering the mass loss between 200 and 500 °C, the relative concentrations of AVO and EHMC in their intercalation compounds were approximately 1% and 3%.

No changes in the DTG peak associated with the decomposition of the clay (~404 °C) were found in either AVO-OB or EHMC-OB, suggesting that the alkyl chain structure of the organophilic bentonite is preserved after the inclusion of sunscreens.

In view of the fact that d_{001} values did not change in either AVO-OB or EHMC-OB, the thermal findings support the hypothesis that the sunscreen molecules occupied the pores between the alkyl chains of bentonite organoclay.

Infrared analysis. The FTIR spectrum of OB showed a peak at 3626 cm^{-1} originating in the OH stretching from Al_2OH (Figure5a). A broad band approximately 3450 cm^{-1} related to the bonded water was also detected in the thermal characterization. Two pronounced bands at 2858 and 2922 cm^{-1} for C-H stretching and a band at 1464 cm^{-1} for a $(CH_3)_4\,N^+$ deformation mode, originating in the alkylammonium ions present in bentonite, were detected. The longitudinal Si–O stretching mode appeared at 1127 cm^{-1} and the OH banding peaks of octahedral layer were observed at 988 and 785 cm^{-1}[16, 19]. These latter peaks indicate the presence of montmorillonite mineral[20].

The infrared spectrum of AVO (Figure 5a) was characterized by several bands between 3000 and 2800 cm^{-1} ascribed to the CH stretching modes of the four methyl groups. The fingerprint region of the FT-IR spectrum is determined mainly by the vibrational mode of the dibenzoylmethanele moiety[21]. The absence of bands at around 1700 cm^{-1}, combined with the split band at around 1590 cm^{-1}, suggests a complete enolization of the β-diketone fragment. The deformation of the methyl groups is associated with the bands at around 1450, 1361, 1257 and 1165 cm^{-1}.

The characteristic FTIR bands of EHMC (Figure 5b)are observed at 3000-2840cm^{-1} for CH, 1702 cm^{-1} for CO, 1600, 1580 and 1462 cm^{-1} for C-C of the benzene and 1165cm^{-1} for CO of the phenol[18].

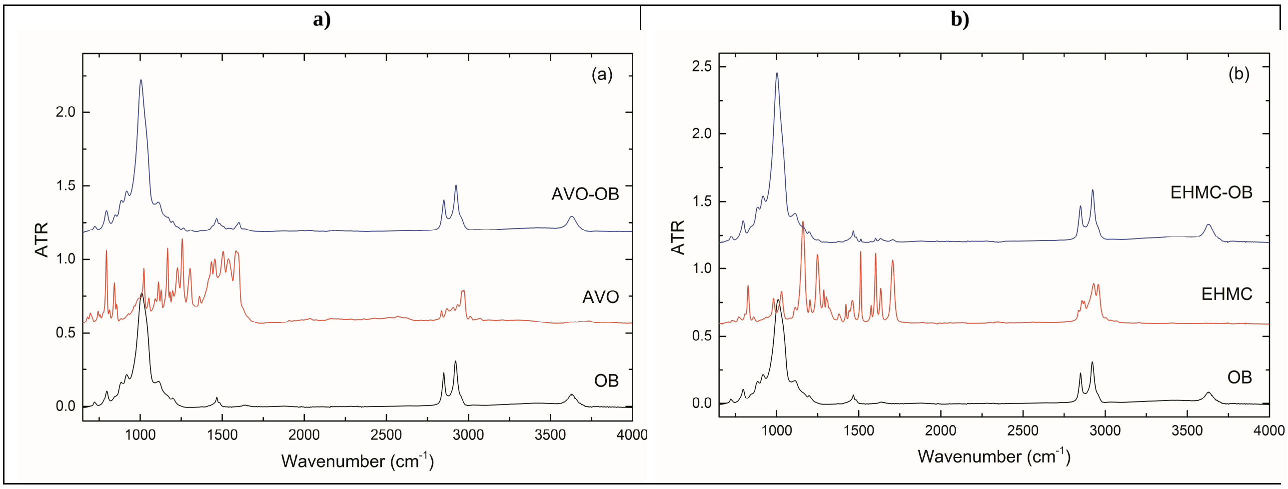
a) b)

Figure 5.FTIR spectra of AVO-OB (a) and EHMC-OB (b)

Despite the low sunscreen concentration in the intercalated compound, the IR bands of the guest molecule can be identified overlapping those of the clay as a minor contribution. The bands ascribed to the sunscreen are wider and exhibit variation in the relative intensities when the intercalation compounds are compared with the pure compounds. This feature may be associated with the loss of the crystalline structure when the sunscreen molecules are intercalated between the alkyl chains, according to the diffractograms.

CONCLUSION

The rapid and simple solution technique was able to obtain intercalation compounds of bentonite sunscreens. The present study demonstrated that the AVO and EHMC sunscreens are intercalated into bentonite, probably in pores between OB alkyl chains, through a well-organized layered structure, as confirmed by the TEM and XRPD analyses.

Furthermore, the thermal analyses confirmed the intercalation and quantified the sunscreen concentrations in the intercalation compounds. All these findings showed the feasibility of the intercalation of the AVO and EHMC compounds with bentonite as a potential system for use in photoprotective skin formulations.

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