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Zeolite-Encapsulated UV-filters: the key for more safe, effective and ecofriendly sunscreens

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1 Abstract

Solar exposure to UVA and UVB radiation is the main cause of skin cancers, whose incidence is nowadays increasing. Thus, the use, empowerment, and research of new sunscreen products containing UV filters is a fundamental topic for the future of material and life sciences.

Ideally, a UV filter should be photostable and convert light into heat, or other forms of energy, once the radiation is absorbed. Nevertheless, if the molecule is photoreactive, it can degrade in other entities of unknown toxicity to human health and the environment. UV filters' stability, and consequently safety, strongly depends on the chemical environment, and particularly on the interaction with other components of sunscreen formulations. Therefore, much effort has been invested in developing more effective and safe sunscreens.

This thesis concerns the preparation and characterization of ZEOfilters, which are hybrid UVfs obtained by the encapsulation of the two organic UV filters octinoxate (OMC), and avobenzone (AVO) into zeolites with MOR, FAU, MFI, and LTL framework topologies, and different Si/Al ratio (low-silica: Na-MOR, LTL, ZSM5-30, 13X-FAU; high-silica: HS-MOR, ZSM5-398, HS-FAU). ZEOfilters were deeply characterized by Elemental Analysis, Thermogravimetric Analysis, UV-visible Spectroscopy, FT-IR spectroscopy, and Synchrotron-X-ray Powder Diffraction. Moreover, the safety of ZEOfilters was evaluated by skin permeation tests, solar exposure tests, and leaching tests into simulated seawater.

The project addressed: i) the optimization of ZEOfilters synthesis; ii) the evaluation of their UV filtering performances; iii) the assessment of the efficacy and safety of ZEOfilters in simulated field conditions; iv) the investigation of host-guest and guest-guest interactions.

A four-step loading procedure was optimized: 1) zeolite dehydration to remove H_2O molecules from channels; 2) UVf loading into the zeolite at 100 °C to promote molecule diffusivity; 3) ZEOfilter washing with acetone to remove unencapsulated UVf molecules; 4) ZEOfilter drying at 60 °C for solvent removal.

The encapsulation was found to be effective, even if strongly variable between different zeolite-UVf combinations. Particularly, OMC was found to be loaded almost evenly in both high- and low-silica zeolites, while AVO is more efficiently trapped in low-silica zeolites compared to their high-silica counterparts.

High silica ZEOfilters, generally display a low UV filtering power and appear colored, possibly due to UVf protonation. Among low-silica zeolites, Na-MOR displays no UVf loading, while the protonated ZSM5-30 presents strong absorption colors alike high-silica zeolites. LTL and 13X-FAU display a high UVf content, an enhanced UV filtering power compared to bare UVfs, and almost complete transparency in the visible range. Thus, LTL and 13X-FAU ZEOfilters were more deeply investigated being the most promising for future applications.

FT-IR experiments and structural refinements were performed on selected samples. FT-IR analysis of HS-MOR/OMC revealed the protonation of OMC (possibly explaining its visible color) together with the inhibition of its trans-cis photoisomerization under UV exposure. In LTL/OMC, FT-IR highlighted a perturbation of the ν(C=O) mode of the OMC carbonyl group, then attributed, by structural refinements, to the carbonyl oxygen bonding to K cations of the LTL zeolite; no protonation of OMC was observed. The major role of carbonyl groups in locking organic compounds into zeolites has been already reported in the literature.

Solar UV exposure tests performed on bare UVfs, and LTL and 13X-FAU ZEOfilters demonstrated high stability of all samples when the compounds were tested independently.

Skin permeation tests were performed on bare UVfs, and HS-FAU, HS-MOR, LTL, and 13X-FAU ZEOfilters in aqueous suspensions, showing a very low permeation through pigskin membrane for all systems (less than 0.2% of the starting amount after 26 hours). The skin permeation of LTL ZEOfilters and bare UVfs in oil-in-water (O/W) emulsions was also tested, leading again to very low values for all tested samples. Results of accumulation in the skin demonstrated that most UVfs (encapsulated or not) accumulate in the stratum corneum and to a lesser extent in epidermis, while the amount in the dermis is negligible (up to 0.06 $\mu g/cm^2$).

In view of future employment, some O/W formulations were prepared with different ZEOfilter content (2 or 20 wt.%) and displayed good rheological properties. The use of ZEOfilters in cosmetics should provide several advantages: i) the UVf-skin interaction should be inhibited by the encapsulation; ii) the UVf-UVf interaction should be prevented by the encapsulation of different UVfs separately; iii) the UVf content of formulation may be reduced thanks to their enhanced filtering power; iv) UVf stabilizers and other co-formulants may be reduced thanks to the improved UVf stability.

During the last decades, UVfs are emerging as a new class of pollutants, especially in the aquatic environment. Leaching tests performed on LTL and 13X-FAU ZEOfilters exhibited very slow but continuous leaching of UVfs (worst-case scenario: 4% after 6 days of testing, for 13X-FAU/OMC). The observed leaching trends do not display an evident flattening up to 160 hours, thus in the future new and more protracted leaching tests should be made.

This thesis is by no means exhaustive of the project, and the development and understanding of these zeolite-based UV filters are still ongoing, and ZEOfilters can be a promising and eco-friendly alternative to traditional UVfs.