자외선차단 화장품 분체소재인 TiO_2가 함침된 일라이트 표면에 코팅된 자연산 버터들의 물성에 대한 연구

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The study of physical properties of natural butters coated on the surface of TiO_2 loaded illites using UV protective powder cosmetics

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Illite is a non-expanding, clay-sized, micaceous mineral. Illite is a phyllosilicate or layered alumino-silicate. Its structure is constituted by the repetition of tetrahedron-octahedron-tetrahedron (TOT) layers [1]. The interlayer space is mainly occupied by poorly hydrated potassium cations responsible for the absence of swelling, even though its structure is constituted by TOT layers. Structurally illite is quite similar to muscovite with slightly more silicon, magnesium, iron, and water and slightly less tetrahedral aluminium and interlayer potassium. The chemical formula is given as $(K,H_3O)(Al,Mg,Fe)_{2(}Si,Al)_4O_{10}[(OH)_2,(H_2O)]$, but there is considerable ion substitution [2]. It occurs as aggregates of small monoclinic yellow to white crystals. Illite occurs as an alteration product of muscovite and feldspar in weathering and hydrothermal environments; it may be a component of sericite [3].

There are both organic and inorganic UV blockers. The organic blockers are also called UV absorbers because they mainly absorb UV rays. Inorganic UV blockers are usually certain semiconductor oxides such as TiO_2, ZnO, SiO_2, and Al_2O_3, for example. Compared with the existing organic UV absorbers, the inorganic UV agents are more preferred because of their unique features including, among others, nontoxicity and chemical stability under both high temperature and UV-ray exposure. However, the mechanism of UV-blocking function of inorganic materials is so far not very clear and researchers hold different views concerning its nature. Take TiO_2, for example: some investigators believe that it provides good UV protection by reflecting and/or scattering most of the UV-rays through its high refractive index [4]. Others believe that it absorbs UV radiation because of its semiconductive properties [5-6]. Still others claim a pile of TiO_2 powder using the nanosize particles for absorb UV radiation, whereas the submicrometer-size particles do very little. On conflicting views, it appears desirable for a thorough investigation on the problem [7].

The aim of our investigation is: (i) to evaluate the UV blocking effect of different loading amount of TiO_2 on illite; (ii) to determine the physicochemical properties and rheological behaviour of TiO_2 on illite; (iii) to put in evidence the need of regulations (standard criteria) for certifying the coated butter characteristics of TiO_2 on illite usable for the formulation of cosmetic material suitable for differentiated pelotherapies and dermatologic applications.

Experimental

TiO_2/illite composite materials with illite and nanosized TiO_2 as starting precursors have been prepared by previous method [8]. The butter coated samples were synthesized by 1%, 3% and 5% addition using Cocoa and Mango butter on TiO_2/illite composite materials. The characterized for crystal structure, chemical bonding and morphology by XRD, FT-IR, and TG-DTA.

Results and Discussion

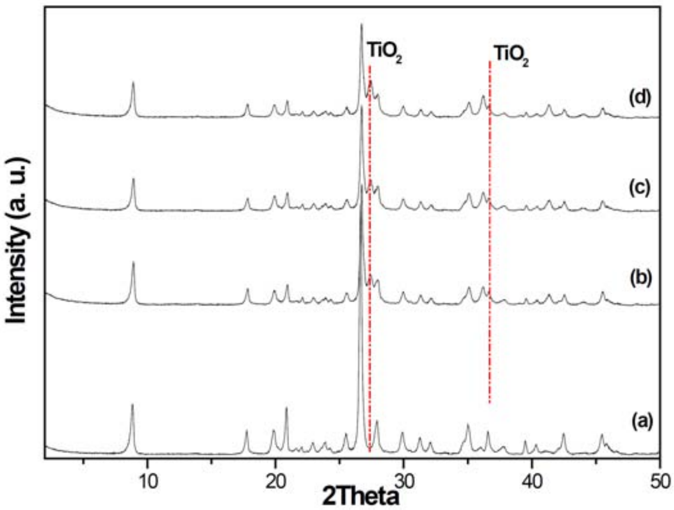

Fig. 1. Powder X-ray diffraction patterns of nanosize TiO_2 loaded on the illite: (a) raw illite, (b) 30wt% TiO_2, (c) 40wt% TiO_2, (d) 50wt% TiO_2.

The X-ray patterns of the TiO_2 loaded on the illite and raw illite shown in Fig. 1. It was observed the transformation sequence as a function of TiO_2 contents. The reflection appeared at 8.8^o (2Θ) with d_{001}-spacing of 10Å. The samples in (b), (c) and (d) by means of increasing TiO_2 contents are shown at $2\Theta = 27.4^o$ and 36.6^o as new peaks with. The result clearly showed evidences of TiO_2 nanosize loaded on the illite.

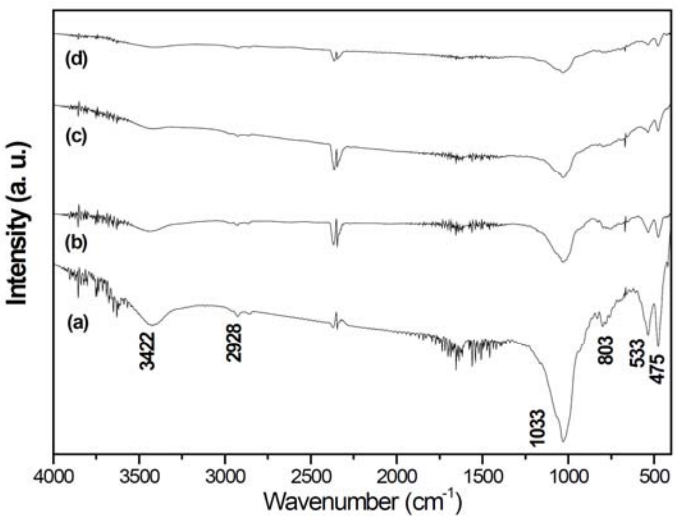

Fig. 2. FTIR spectra with contents cocoa butter (CB) coated to nanosize 50wt%TiO_2/Illite and raw illite: (a) raw illite, (b) 1%CB, (c) 3%CB, (d) 5%CB.

Inner hydroxyl groups, lying between the tetrahedral and octahedral sheets, give the absorption near 3620cm^{-1}. The other three OH groups reside at the octahedral surface of the layers and form weak hydrogen bonds with the oxygens of the Si-O-Si bonds on the lower surface of the next layer. A strong band at 3695cm^{-1} is related to the in-phase symmetric stretching vibration, two weak absorptions at 3669 and 3653cm^{-1} are assigned to out-of-plane stretching vibrations The combination band of OH in water molecules appears at 1910cm^{-1} and that of structural OH appears at 2200-2400cm^{-1}, depending on the environment. Both of them are decreasing for the coated samples. The water is consumed during the hydrolysis, but it is again present in the coated samples stored in air, and therefore no clear statements can be made based only upon the variation of these peaks. For the coated samples, CH stretching overtones appear at 1675 and 1690cm^{-1} and the CH combination mode is present at 2300cm^{-1}. A shoulder appears at 2250cm^{-1} in the spectra of the modified samples.

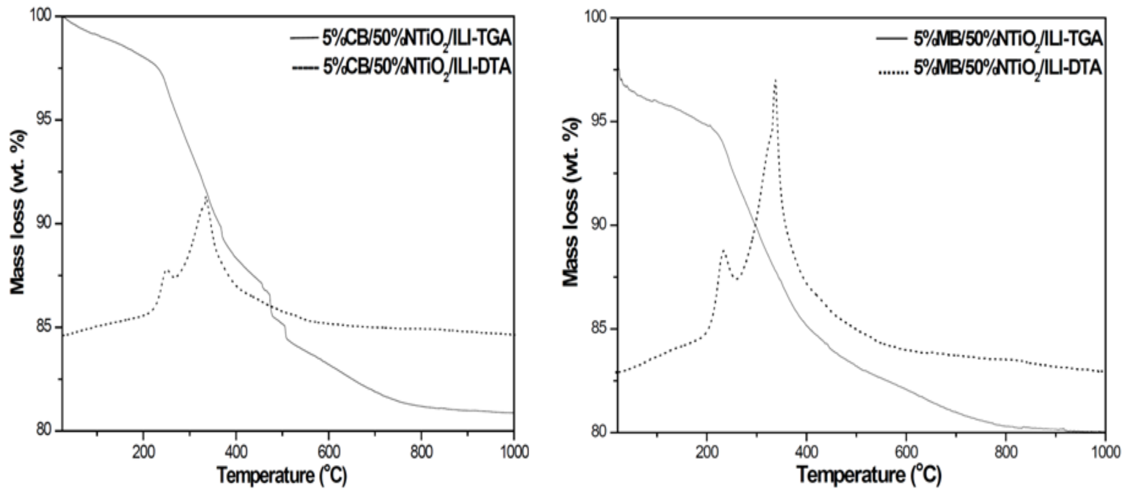

Fig. 3. TG-DTG curve measurement for cocoa butter (CB) and mango butter (MB) coated to nanosize 50wt% TiO_2/Illite.: (a) 5%CB/50%NTiO_2/ILI-TG-DTA (b) 5%MB/50%NTiO_2/ILI-TG-DTA

This absorption could be assigned bridging OH, of the type Al-OHAl, or between three Al, environments characteristic in our case to coated butters.

The TG-DTA curve of the cured sample as shown in Fig. 3 demonstrates very small weight loss in the temperature range of 150-200^oC which are characteristic of the desorption of physically adsorbed water molecules. There is a steady weight loss between 150 and 450^oC and one exothermic peak is observed at 330^oC, which can be attributed to the release of chemically bounded water (around 200^oC) and the decomposition of the organic components (around 330^oC). DTA curve demonstrates an exothermic peak near 400^oC, which can be associated with the crystallization process of an amorphous oxide. After 700^oC only 17.80% weight loss has observed which implies about rigid and integrated polymer network formed by illite and coupling agents.

Conclusion

The natural butter coating was successfully carried out on TiO_2 nanoparticles loaded on illte. In butter coated TiO_2/illite, island-like structured rutile TiO_2 aggregates were strongly anchored and well dispersed on the flat surface of illite. The butter coating extent was enhanced with TiO_2 nanoparticle loaded on illite. In TGA-DTA, coating butters were observed to be bonded successfully with TiO_2 by chemical bonding.

Acknowledgements

This study was supported by a grant of the Korea Healthcare Technology R&D Project, Ministry of Health & Welfare in Republic of Korea (Grant No. A103017).

References

1. Eslinger, E., P. Highsmith, D. Albers, B. deMayo, *Clays and Clay Minerals*, **27**, 327 (1979).
2. M. Rieder, G. Cavazzini, Y. D’Yakonov, V.A. Frank-Kamenetskii, G. Gottardi, S. Guggenheim, P.V. Koval, G. Muller, A.M.R. Neiva, E.W. Radoslovich, J.L. Robert, F.P. Sassi, H. Takeda, Z.Weiss, D.R.Wones, *Can. Mineral.*, **36**, 905 (1998).
3. Nadeau, P., D. Bain, *Clays and Clay Minerals*, **34**, 455 (1986).
4. Bohringer, B., *Proceedings of the 37th International Man-Made Fibres Congress, Dornbirn, Austria*, **9**, 1031 (1998).
5. Thiry, M. C., AATCC Rev, **6**, 13 (2002).
6. Wedler, M., Hirthe, B., *Chem Fibers Int*, **49**, 528 (1999).
7. Zhang, L., Mou, J., *Nano-materials and Nano-structure*; Science Press: Beijing, 84 (2001).
8. M. H. Kim, S. N. Kim, Gi-. Kim, S-. Jang, H-. Kim, Y. Song, S. Yi, C-. Lee, *Theories and Applications of Chem. Eng.*, **17**, 1939 (2011).