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Titanium dioxide as a safe additive to sunscreen emulsions

Marcin Janczarek*, Waldemar Szaferski

Poznan University of Technology, Institute of Chemical Technology and Engineering, Berdychowo 4, 60-965 Poznan, Poland

Titanium dioxide with its ability to be a UV light blocker is commonly used as a physical sunscreen in the cosmetic industry. However, the safety issues of TiO_2 application should be considered more in-depth, e.g., UV light-induced generation of reactive oxygen species which can cause DNA damage within skin cells. The proper modification of titanium dioxide to significantly limit its photocatalytic properties can contribute to the safety enhancement. The modification strategies including the process conditions and intrinsic properties of titanium dioxide were discussed. The selected examples of commercially available TiO_2 materials as potential components of cosmetic emulsions dedicated for sunscreens were compared in this study. Only rutile samples modified with Al_2O_3 and/or SiO_2 showed inhibition of photocatalytic activity.

Keywords: sunscreen emulsions, titanium dioxide, photocatalysis

1. INTRODUCTION

Sunscreen cosmetics provide protection against adverse effects of ultraviolet irradiation: UVB (290–320 nm) and UVA (320–400 nm). Titanium(IV) oxide (titanium dioxide, titania, TiO_2) belongs to the group of compounds that can be classified as inorganic UV light blockers for sunscreen applications. In addition to TiO_2, this group also includes zinc oxide. There is also the group of organic UV-filters such as oxybenzone. Sunscreens based on inorganic blockers are characterized with absence of skin irritation and sensitization, inertness of these additives and limited skin penetration (Smijs and Pavel, 2011). For titania one can distinguish three main crystalline forms: anatase, rutile and brookite. All forms have high refractive index (especially rutile) that allows good UV light reflection and scattering. Furthermore, TiO_2 is a semiconductor with bandgap energy of about 3 eV, therefore its absorption properties are limited to UV range of irradiation. In general, the UV attenuation results from both reflection and scattering of UV and visible light and from absorption of UV irradiation.

As titania is a semiconductor, any photon with energy higher than the bandgap (UV light) will be absorbed resulting in the formation of electron – hole pairs. They undergo a series of complex redox reactions that yield to the formation of reactive oxygen species (ROS) such as hydroxyl radicals, superoxide radicals and singlet oxygen (Carp et al., 2004). The presence of ROS is the effect of photocatalytic properties of titanium

* Corresponding author, e-mail: marcin.janczarek@put.poznan.pl

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dioxide. In many possible applications of TiO_2 this phenomenon is beneficial, e.g., in the case of self-cleaning surfaces. However, for sunscreening activity this effect has been found to be detrimental (Carlotti et al., 2009; Lewicka et al. 2013; Serpone et al., 2007; Smijs and Pavel, 2011; Wakefield et al., 2004). This issue, directly influencing sunscreen safety, is often undervalued. The presence of irradiated TiO_2 in contact with skin can cause various adverse effects, e.g., phototoxicity to skin fibroblasts, photooxidation of cellular DNA and RNA. Genotoxicity, cytotoxicity and the enhancement of UV-induced damage in an epidermal skin have been correlated with titania nanoparticles (Carlotti et al., 2009; Livraghi et al., 2010). Undesirable influence of photocatalytic properties of titania can be also expressed by the mineralization of organic components in sunscreens and subsequently decreasing of sun protection efficiency (Ricci et al, 2003). Furthermore, the size of semiconductor nanoparticles (< 100 nm) allows their easy penetration through the stratum corneum of the skin and subsequent transfer into the skin's deeper layers (Cross et al., 2007; Regiel-Futyra et al. 2015).

Therefore, the application of modified TiO_2 with inhibited photocatalytic activity is an important purpose. The first strategy of modification is coating of titania particles with inorganic (e.g., SiO_2, Al_2O_3 and/or organic (e.g., alkoxy titanates, silanes, methyl polysiloxanes) substances which separate the surface of TiO_2 from oxygen and water (Bai et al. 2017; Cheepborisutikul and Ogawa, 2021; Guo et al. 2017; Guo et al. 2018; Morsella et al., 2016; Siddiquey et al., 2008; Slomberg et al., 2020; Tiano et al., 2010; Xiao et al., 2013; Yu et al., 2018). The second approach is thermally assisted inactivation of titania (Serpone et al., 2006). The application of polymer coatings with antioxidant properties has been also considered (Lee et al., 2007; Morsella et al., 2016). Another strategy to inactivate titanium dioxide is to perform its modification with vanadium or manganese (Wakefield et al., 2004). Titania modification oriented for the reduction of ROS formation can occur also with non-metals such as carbon (Livraghi et al., 2010). The conditions of modification and other physical and structural properties of TiO_2 (such as phase content, particle size, particle morphology) are the key-points to obtain material with reduced photocatalytic activity. For example, for carbon-modified titania there are many reports with opposite effect, where ROS formation was significantly improved (Ghumro et al., 2022). Similar observations have been made with the application of metal oxides such as SiO_2 (Urkasame et al., 2018). Another underestimated aspect is the influence of prepared titania-based materials on the properties of cosmetic emulsions. The main purpose of this work was to compare five commercially available TiO_2 materials (including modified samples) as candidates for cosmetic emulsion additives with sunscreen function. An assessment of suitability to meet the requirements presented above (inhibition of photocatalytic activity) will be performed.

2. MATERIALS AND METHODS

The following TiO_2 samples were selected in this study:

- Aeroxide® P25 (Evonik, Germany) – mixture of anatase (80%) and rutile (20%),
- anatase nanopowder (Sigma-Aldrich, Germany) – nanosized pure anatase particles,
- Tytanpol® R-210 (Z.Ch. Police S.A., Poland) – rutile, surface modified with Al_2O_3 (3%), SiO_2 (1%) and organic compounds with hydrophilic character,
- Tytanpol® R-001 (Z.Ch. Police S.A., Poland) – rutile, surface modified with Al_2O_3 (3%) and organic compounds with hydrophilic character,
- Tytanpol® RS (Z.Ch. Police S.A., Poland) – rutile, surface modified with Al_2O_3 (1%) and organic compounds with hydrophobic character.

The commercially available lotion was used in this study (Isana, Germany). The main ingredients of the lotion were water, glycerin, isopropyl palmitate, cetearyl alcohol, glyceryl stearate citrate, dicaprylyl ether, hydroxypropyl starch phosphate, tocopherol, tocopheryl acetate, caprylyl glycol, xanthan gum, benzyl salicylate, phenoxyethanol, potassium sorbate, sodium hydroxide. The emulsions containing of 1, 2 and 3 wt% of titania were prepared. The homogenizer was used with the rotational speed of 166 rpm. The homogenization process was carried out for 15 minutes.

The photocatalytic activity of the considered titania samples (P25, anatase, R-210, R-001 and RS) was evaluated in the aqueous suspension system with 4-chlorophenol (4-CP, Aldrich) as a model organic compound. A 50 W UV-LED lamp (Bridgelux) with wavelength of 395 nm was used as a light source. The suspension of 100 mg of photocatalyst in 100 mL of 4-CP aqueous solution (10 mg L^{-1}) was placed into the glass photoreactor. Subsequently, the resultant suspension system was mixed in the dark (30 min) to establish adsorption/desorption equilibrium. Then, the UV-LED lamp was switched on and the reaction mixture was irradiated. Every 30 min (up to 360 min), 3 mL of the suspension was collected and filtered through a syringe filter (Macherey–Nagel). The 4-CP concentration in the filtrate was monitored using a UV-Vis spectrophotometer (V-750, Jasco) through its absorbance at 225 nm.

The base lotions and the resulting emulsions were visually analyzed using the microscope (Nikon Eclipse 50i equipped with Opta-Tech camera).

3. RESULTS AND DISCUSSION

3.1. Effect of TiO_2 surface modification on the photoinduced formation of reactive oxygen species (ROS)

The photocatalytic properties of considered TiO_2 materials were tested in relation to photooxidation of 4-chlorophenol as a model compound. In relation to photoabsorption characteristics, titanium dioxide efficiently absorbs UV light causing electron-hole separation (Eq. (1)) and subsequent generation of ROS such as hydroxyl ($HO^{\bullet}$) and superoxide radicals ($O_2^{\bullet-}$), and hydrogen peroxide (Eqs. (1)–(3)), which are responsible for initiation of oxidative reactions, such as 4-CP photooxidation (Eq. (4)). Hydroxyl radicals are formed on the surface of TiO_2 by reaction of holes in the valence band (h^+_{VB}) with adsorbed H_2O or hydroxide (Eq. (3)). The photogenerated electrons from the conduction band (e^-_{CB}) participate in the generation of superoxide radicals (Eq. (2)). Produced ROS have enough oxidation potential for oxidization of organic compounds and their final mineralization (Carp et al., 2004).

$$TiO_2 + h\nu \longrightarrow e^-_{CB} + h^+_{VB} \tag{1}$$

$$e^-_{CB} + O_{2(ads)} \longrightarrow O_2^{\bullet-} \tag{2}$$

$$h^+_{VB} + OH^-_{(ads)} \longrightarrow HO^{\bullet} \tag{3}$$

$$ClC_6H_4OH + 6.5O_2 \xrightarrow[TiO_2]{h\nu} 6CO_2 + HCl + 2H_2O \tag{4}$$

Figure 1 and Table 1 show the results of photocatalytic activity tests under UV irradiation of analyzed TiO_2 samples. Significant reaction rate of 4-CP photodegradation was observed for P25 and anatase. The surfaces of these samples were unmodified. The mixture of anatase and rutile (P25) determines the highest activity. P25 is a generally accepted reference titania sample for photocatalytic activity studies. Pure anatase with nanosized particles exhibits less photooxidation efficiency in the considered reaction.

Different observation was performed for Tytanpol samples with modified surface. Almost no photocatalytic activity was reported for R-210, R-001 and RS titania samples. These results confirm the concept that the surface modification of titania with SiO_2 or/and Al_2O_3 can be crucial for photocatalytic activity inhibition (Carlotti et al., 2009; Tiano et al., 2010). In the case of Tytanpol samples, the existing layer on the TiO_2

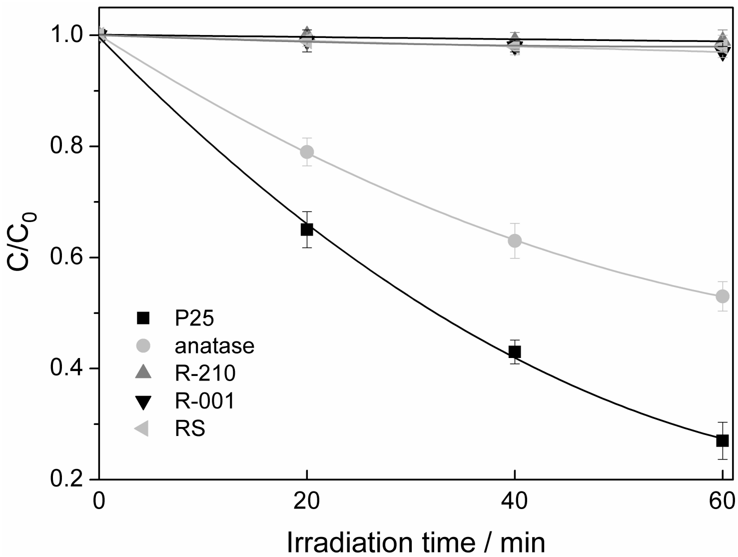

Fig. 1. Photocatalytic oxidation of 4-CP under UV irradiation in the presence of P25, anatase, R-210, R-001 and RS titania samples. Initial concentration of 4-CP: C_0 = 10 mg L^{-1}. Error bars represent the standard deviations of duplicate runs

Table 1. Reaction rates for photocatalytic oxidation of 4-CP under UV irradiation

Sample name	Reaction rate [µmol h^{-1}]
P25	56.70
anatase	36.54
R-210	0.78
R-001	2.23
RS	1.55

surface consisting of Al_2O_3 or/and SiO_2 is responsible for effective suppression of ROS generation. If the titania particle is fully covered by a stable, non-reactive layer that inhibits any contact between the TiO_2 surface and oxygen/water, the inhibition of ROS production occurs and there will be a much reduced hazard, if any. Very important factor influencing efficiency of silica/alumina layer is its thickness (Cheepborisutikul and Ogawa, 2021). Complete inhibition of photocatalytic activity for Tytanpol samples means that this layer thickness seems to be enough. On the other hand, pure white color of these samples confirms that optical properties were not disturbed by the silica/alumina modification, therefore this material can be used as a UV filter. Furthermore, obtained results also show that the type of surface character – hydrophilic (R-001 and R-210) and hydrophobic (RS) – does not influence directly photocatalytic activity and the efficiency of its inhibition is on the same level.

3.2. Properties of emulsions containing surface modified TiO_2

Using a homogenizer, the emulsions with the addition of four considered TiO_2 in the concentrations of 1, 2 and 3 wt% were prepared. In comparison with base emulsion without titania addition (Fig. 2), in the microscopic images one can observe the presence of TiO_2 agglomerates noticeable as dark clusters (Fig. 3–5), although titania was not visible with the naked eye and it did not influence the color of resultant formulations. In the case of P25 and R-001, the increase of their content to 3 wt% worsened the stability

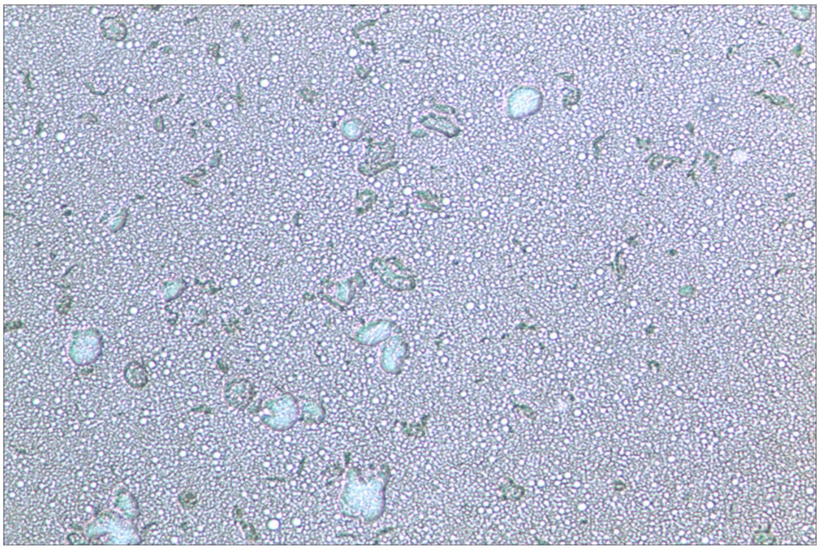

Fig. 2. Microscopic image of base emulsion (no TiO_2 addition)

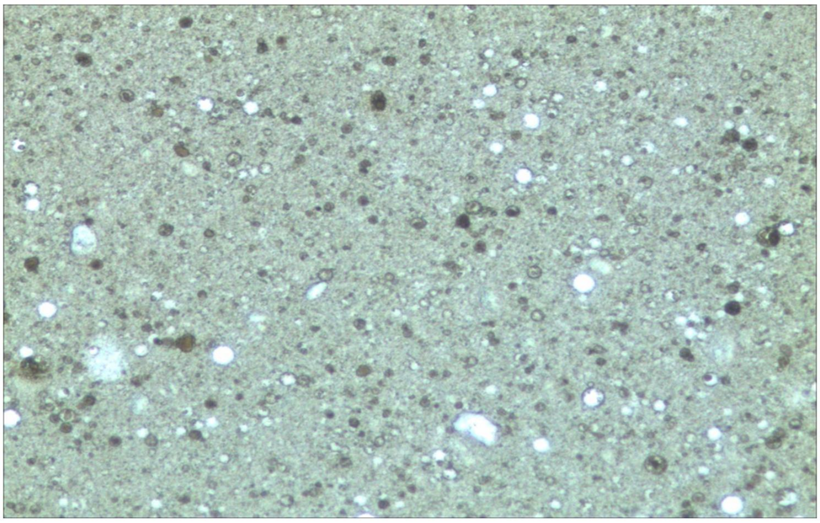

Fig. 3. Microscopic image of emulsion with 2 wt% P25 addition

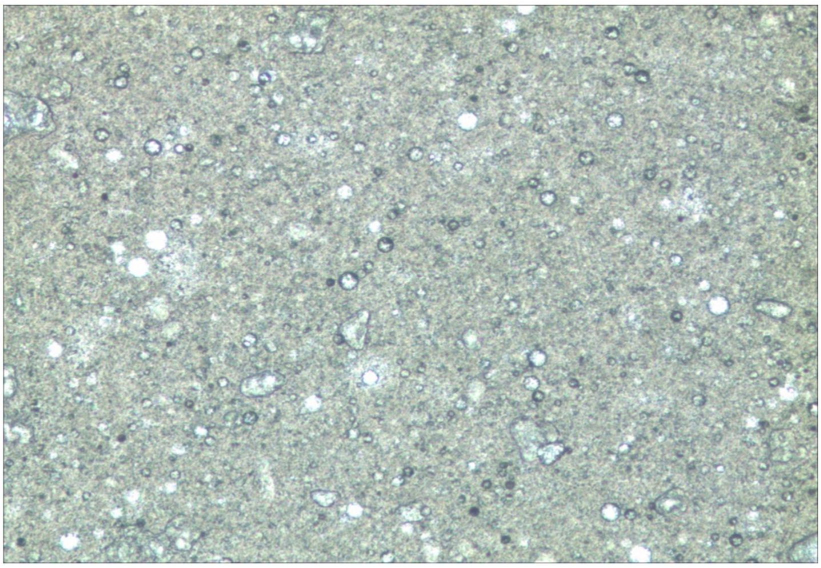

Fig. 4. Microscopic image of emulsion with 2 wt% R-001 addition

of emulsion. As the content of titania additives introduced into the formulations increased, the number of TiO_2 agglomerates increased, but their size remained the same. Taking into consideration the use of RS and R-210 additives, deterioration of resultant emulsion stability was not reported also for the titania content of 3 wt%. The difference in the emulsion stability between R-001 and RS titania samples can be explained by the wettability character of their surfaces. RS sample was additionally modified with organics of hydrophobic character. On the other hand, R-001 sample was modified with organics introducing to titania surface a hydrophilic character. The proper adjusting of wettability of TiO_2 surface can be a crucial factor for obtaining a stable sunscreen formulation.

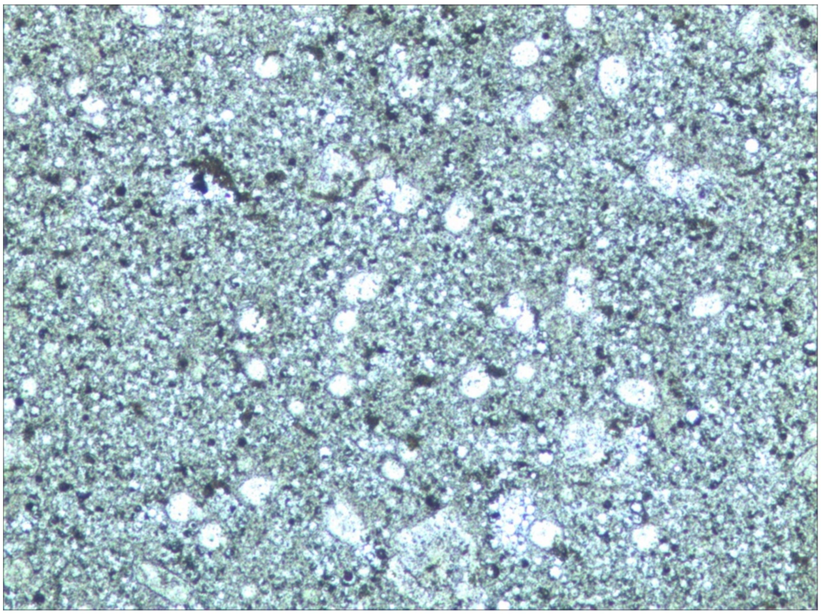

Fig. 5. Microscopic image of emulsion with 2 wt% RS addition

4. CONCLUSIONS

For the first time, three types of commercially available Tytanpol titania pigments with modified surface were considered as candidates for cosmetic emulsion additives introducing a sunscreen function. It has been shown that the presence of surface coating agents such as Al_2O_3 or/and SiO_2 is crucial for blocking reactive oxygen species formulation and subsequently contributes to the inhibition of photocatalytic activity of TiO_2 materials. This strongly reduces the risk of their application, e.g. DNA damage within skin cells under solar irradiation. The characterization of obtained emulsions showed that the factor of intrinsic properties of titania additives such as surface wettability should be also considered in the discussion about the suitability of sunscreen agents in the preparation of stable cosmetic emulsions.

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